THERMODYNAMICS

OF

REVERSIBLE CYCLES IN GASES AND SATURATED VAPORS.

FULL SYNOPSIS OF A TEN WEEKS' UNDERGRADUATE COURSE OF LECTURES DELIVERED BY

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PREFACE.

My dear Mr. Osterberg:

It was quite a pleasure to examine your carefully worked out notes on my lectures. I agree with you in the opinion that the publication of these notes will be of much service to your classmates and probably to others who may be interested in the elementary features of thermodynamics.

Very sincerely yours,

M. I. Pupin.

Columbia College, New York,
December 20, 1893.

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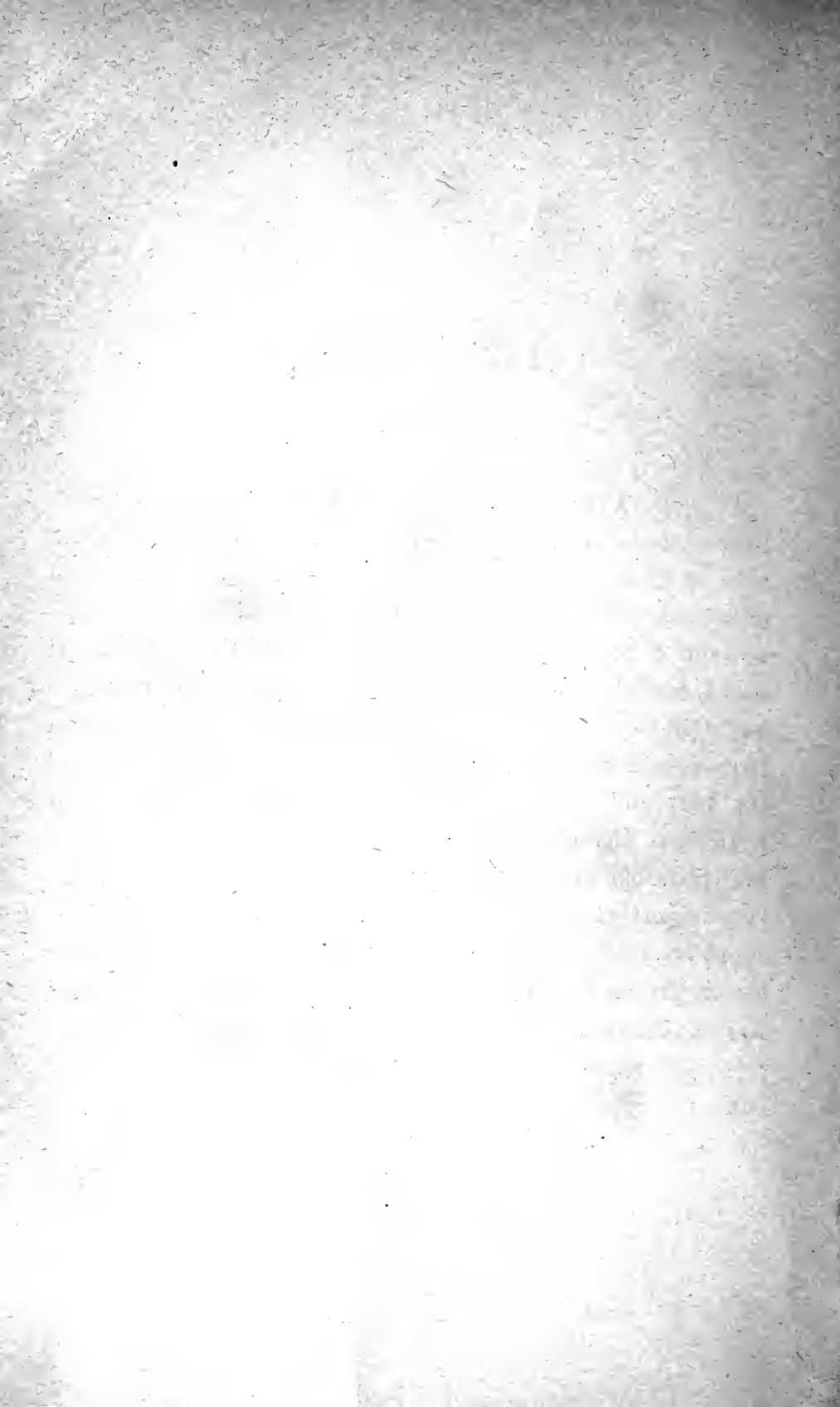
INTRODUCTION.

IN this course on *Theoretical Thermodynamics* we shall limit our discussion to those features of the science which have a direct bearing upon the science of Caloric Engineering. The course forms, therefore, a theoretical introduction to the practical course on Heat Engines. It seems desirable, however, to mould our discussion in such a way that it will serve at the same time the very important purpose of forming an introduction to the study of some of the best and most complete works on the subject. The work of R. Clausius (*Die mechanische Wärmetheorie*) is and very probably will always remain the classical treatise on this very important branch of exact sciences. We shall, therefore, adopt the mathematical notation and follow as closely as practicable the method of discussion which is given in this great work of Clausius, who, as you will presently see, is one of the principal founders of the beautiful science of thermodynamics.

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THERMODYNAMICS

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I.

NATURE OF HEAT AND THE MATHEMATICAL STATE-MENT OF THE FIRST LAW OF THERMODYNAMICS.

The Science of Thermodynamics investigates the formal or quantitative laws which underlie all physical processes by which the caloric state of material bodies is changed.

By physical process we simply mean any one of the almost infinite variety of ways by which nature transforms one form of energy into another, or one form of matter into another. Heat is developed in almost every physical process, owing principally to the presence of passive or frictional resistances, unavoidable in material systems.

The first question to be considered is: *What is heat?* It certainly must be one of the two fundamental physical quantities, that is, *it must be either a form of matter* or a

form of energy. In the first case it will be subject to *the principle of conservation of matter,* and in the second case it will be subject to *the principle of conservation of energy.*

According to the old hypothesis heat is a substance ; but since the weight of a body is independent of its temperature, the heat substance, *the so-called Caloric, had to be supposed to be imponderable.*

The experiments of *Sir Humphry Davy* (1799*) and of *Rumford* (1798 †) showed, however, that, 1st, the *latent heat* contained in a given body *could be increased,* and, 2d, the *temperature of a body could be changed without a change in the quantity of heat in the surrounding bodies.*

The first was shown by Davy's experiment of melting two pieces of ice by rubbing them one against the other ; the second was shown by Rumford's experiment, in which heat was developed by friction, which accompanies the boring of metals. These experiments gave the death-blow to the old or substance theory of heat.

They showed not only that heat cannot be a substance, but that on the contrary it has all the physical characteristics of the other fundamental physical quantity, which we call energy. As such it must be subject to the principle of conservation of energy. *Joule was the first to show that heat and mechanical work are not only convertible into each other, but that the*

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* Essay on Heat, Light, and the Combinations of Light, with a new Theory of Respiration. Experiments II. and III.

† Count Rumford's essay on " An Inquiry concerning the Source of Heat which is excited by Friction," read before the Royal Society, January 25th, 1798. See Memoir of Sir Benjamin Thompson, Count Rumford, with notices of his Daughter, by George Edward Ellis.

ratio of conversion is constant (1839–1844).   Later on he extended this relation to other forms of energy, like chemical energy, etc.   By these experiments Joule not only proved that heat is a form of energy convertible into mechanical or any other form of energy at a constant ratio, *but he also furnished the first exact experimental basis for the general principle of conservation of energy*, first enunciated by *Julius Robert Mayer* about the same time (1842).   It was, however, clearly stated in its most general form and mathematically elucidated by *Helmholtz in* 1847.

The principle of Conservation of Energy can be stated as follows : *Energy cannot be created nor can it be annihilated by any physical processes which our mind can conceive.*   The energy contained in an isolated material system must, therefore, remain constant, although all sorts of changes may be taking place within the system.   These changes, however, will consist in a transformation of one form of energy into another or one form of matter into another *without loss.*

When the energy of a body or system of bodies is changed in amount, then the change is due to the *transference of energy from external bodies to the system considered, or vice versa.   In the first case, work is done upon the system; in the second, the system does work upon external bodies.*

If we heat a body, one part of the heat energy put into it will appear as heat, another part as work done against external forces, like surface pressure, and another part as potential energy overcoming the internal forces, like forces of cohesion, chemical affinity, etc.   The common unit of measure of all these forms of energy is the unit of mechanical

work, that is, the kilogramme-meter, *The unit of heat is one klgr. calorie.*

Def.—*One klgr. calorie is the heat necessary to raise the temperature of a klgr. of a standard body one degree.* The standard body being pure distilled water at 4° C., and at normal pressure (760 mm.).

The *mechanical equivalent of heat is the number of klgr. meters which must be spent to generate that much heat.*

It was found by experiment that one klg. calorie = 424 klg. m. (very nearly). The most distinguished experimentalists in this line being Robert Mayer, Joule, Hirn,[*] Rowland.

To express, say, 890 klgr. meters in calories, divide 890 by one J (" Joule ") or 424 (J being the symbol of the mechanical equivalent of heat).

Statement of the First Law of Thermodynamics for a Particular Class of Physical Processes.

We will now limit ourselves to that class of bodies and processes in which the external work done is mechanical work, and in that class of processes we shall select those processes where the mechanical work is done in overcoming a certain amount of pressure on the surface of a body to which we apply the heat, and consider that the pressure is uniform and normal at all points of the surface.

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[*] Hirn, Recherches sur l'équivalent mécanique de la chaleur, p. 20; Also, Théorie mécanique de la chaleur, 2d edition, part 1st, p. 35.

Expression for External Work due to Infinitesimal Expansion.

Consider an infinitesimal area of the surface du square meters ; if the pressure per sq. m. is p kg., the total pressure is pdu. Now suppose the body to expand, overcoming the surface pressure: the work done by the act of displacing du is equal to the normal displacement dn meters times the pressure, that is $pdudn$ kg. meters.

To find the total work done over the whole surface, we must integrate (remembering that p is uniform all over the surface).

$$\int pdudn = p\int dudn = pdv.$$

That is to say, *for infinitely small increments of volume,* during which the surface pressure may be considered constant, the external work is equal to the surface pressure multiplied by the increment in volume.

Intrinsic Energy and Co-ordinates of a Body.

Let us now communicate an infinitely small quantity of heat dQ to a body. Experience tells us that the following changes in the body may be looked for: change in temperature, internal aggregation, chemical constitution, electrical and magnetic state, volume, etc., etc. If we now call the energy which a body contains in consequence of its temperature, internal aggregation, chemical constitution, electrical and magnetic state, etc., etc., the *intrinsic energy* of the body, and denote it symbolically by the letter U, and if we denote by W

the external work which a body does against the surface pressure in expanding from a given volume to some other volume, then it is evident that the above changes in temperature, aggregation, chemical constitution, electrical and magnetic state, volume, etc., etc., imply a certain small change dU in the intrinsic energy and a certain small external work dW. *According to the Principle of Conservation of Energy the mechanical equivalent of dQ is equal to the mechanical equivalent of dU plus the mechanical equivalent of dW.* Hence

$$dQ = dU + dW.$$

This is the most general form of the first law of thermodynamics. It is a formal statement of the Principle of Conservation of Energy for processes which involve a transformation of a certain amount of heat.

Experimental Physics and Experimental Chemistry teach us how to measure the physical quantities by means of which we describe the various states of physical bodies, these quantities being temperature, forces of cohesion, chemical affinity, quantities of various chemical elements contained in a body, magnetic and electrical intensity in the various parts of the body, volume, pressure, etc., etc. The energy contained in a body depends on its state and not on the processes by means of which the body has been brought into that state. Hence the physical quantities just mentioned which describe the state of the body will also determine completely the value of the intrinsic energy U which the body has in that state. *This is what we mean when we say that U is an analytical function of the above physical quantities.*

The external work which a body does against surface press-
ure while expanding from a given volume to some other
volume may or may not be independent of the process by
means of which this expansion is effected. To be general, we
shall suppose that it is not independent, that is to say, we shall
suppose that W is such a function of the physical quantities
which define the state of the body, that in passing from one
set of values of these quantities to another set the change in
the value of W will depend on the physical processes by means
of which we passed from the first to the second set.

This will be illustrated further on by actual examples. The
physical quantities, like temperature, magnetic and electrical
intensity, pressure, volume, chemical affinity, quantity of mat-
ter, etc., which define the state of a body are called *the co-
ordinates of a body.* We say then that U and W are functions
of the co-ordinates of the body.

It is evident that the more complex the state of a body the
more co-ordinates shall we need to describe its state. *For
the present we shall limit ourselves to those physical bodies
and physical processes in which temperature, volume, and
pressure suffice to describe completely the state of the body,
and the processes by means of which that state is varied.*

U will therefore be a function of the pressure p, the
volume v, and the temperature t; the same is true of W.

We shall measure p in kilogrammes per square meter, v
in cubic meters, and t in degrees centigrade.

It must be observed, however, that these three co-ordi-
nates of the body are not independent of each other. Thus
the surface pressure and the temperature of a body being
given, its volume is also determined. Varying the pressure

without varying the temperature, we can pass from any volume
to any other volume (within certain definite limits).

We can therefore express U in terms of two of these. In
what follows U will be considered a function of t and v unless
the contrary is stated.

We shall therefore have in the case of these bodies and
these physical processes

$$dQ = \frac{\partial U}{\partial t} dt + \frac{\partial U}{\partial v} dv + dW.$$

Since the pressure is normal and **uniform and constant for**
infinitely small variations of volume and temperature,

$$dW = pdv;$$

$$\therefore \ dQ = \frac{\partial U}{\partial t} dt + \left(\frac{\partial U}{\partial v} + p \right) dv.$$

Hence the first law of thermodynamics in the case of bodies
and processes, which we are considering, says : If we com-
municate an infinitely small amount of heat to a body
under pressure, a part of the heat is used up in increasing
the internal energy of the body, part of which is potential
and part heat energy, and the rest appears as mechanical work
done against the surface pressure.

If a finite quantity of heat Q is communicated to a body,
causing the same to pass from a given state, in which its tem-
perature is t_1, surface pressure p_1, and total volume v_1, to an-
other state, in which these quantities are t_2, p_2, v_2, then

$$Q = U_2 - U_1 + \int_1^2 pdv.$$

but it does not follow that $\frac{dU}{dt}dt = dH$ and $\frac{dU}{dv}dv = dJ$

That is, the total quantity of heat is equal to the total increment of internal energy plus the total external work. The increment in internal energy is due to two changes: 1st, change of temperature; 2d, change in the arrangement of matter in the body. The first change produces a variation in the thermometric heat; the second, in the latent heat of the body.

If pressure is constant, then external work $= p(v_2 - v_1)$. But since this is not always the case, we must, in order to find the numerical value of the integral $\int p\,dv$, consider first the law of variation of p with v.

For infinitely small variations of volume the pressure can be considered constant.

II.

APPLICATION OF THE FIRST LAW OF THERMODYNAMICS TO PERFECT GASES.

We pass now to the application of the First Law of Thermodynamics to the study of the simplest thermodynamic processes that can be performed upon the simplest class of physical bodies, that is, we pass to the application of the First Law of Thermodynamics to the study of the process of expansion and compression of *perfect gases*.

These bodies may justly be considered the simplest bodies, because *experimental research tells us that* their co-ordinates describe the state of these bodies by the simplest formal relations that we know of, namely,

Relation (1) contains what is known as Boyle's law, viz.:

$$p_1 v_1 = p_2 v_2. \quad \cdots \quad \cdots \quad (1)$$

That is to say, if a given quantity of a perfect gas, say a kilo-

gramme of dry air at a given temperature, occupies a volume v_1 when it is under a pressure p_1, then the same quantity of the gas at the same temperature when it is under pressure p_2 will occupy the volume v_2 as given in above equation.

This relation is true for a large number of gases within a large interval of pressure and temperature.

Relation (2) contains what is known as the Mariotte–Gay-Lussac law, viz.:

$$pv = p_0 v_0 (1 + \alpha t). \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Here p is pressure in kg. per square meter and v is volume in cubic meters of a unit weight (that is a kilogramme) of a perfect gas when it is under the pressure p and when its temperature is t deg. centigrade above the standard freezing-point. p_0 and v_0 denote the corresponding quantities of the same weight of the gas at the freezing-point. α is called the temperature coefficient of expansion. It is found to be very nearly constant for all temperatures within a large interval, and to be $= \frac{1}{273}$ (very nearly) for all perfect gases.

The Mariotte–Gay-Lussac law can also be written

$$pv = \frac{p_0 v_0}{273}(273 + t) = \frac{p_0 v_0}{273} T = RT.$$

Here T *is called the absolute temperature* of the gas and R is a constant which depends on the nature of the gas. It can be calculated for every gas from experimental data, as will be shown presently.

Choosing T and v as the co-ordinates of the gas, we have

$$dQ = \frac{\partial U}{\partial T} dT + \frac{\partial U}{\partial v} dv + p \, dv.$$

On the Rates of Variation of the Intrinsic Energy of a Perfect Gas.

When a small quantity of heat dQ is communicated to a body, then a part of it will appear as an increment in the intrinsic energy of the body, and the other part will appear as external work.

The first part consists of two terms, namely, $\frac{\partial U}{\partial T} dT$ and $\frac{\partial U}{\partial v} dv$. Now $\frac{\partial U}{\partial T} dT$ is the increment of intrinsic energy due to the increase of the body's temperature by dT. The factor $\frac{\partial U}{\partial T}$ is the rate at which internal energy varies with the temperature, *the volume being constant*. If that rate were constant, then the factor $\frac{\partial U}{\partial T}$ would mean the increment of internal energy due to a rise of temperature of 1°. This part $\frac{\partial U}{\partial T} dT$ appears as sensible heat of the body, i.e., heat which can be measured by a thermometer. The other part $\frac{\partial U}{\partial v} dv$ is the increment of intrinsic energy due to the change of the body's volume, the temperature remaining constant. The factor $\frac{\partial U}{\partial v}$ is the rate at which this increment takes place; if this rate remained constant for finite variations of volume, then $\frac{\partial U}{\partial v}$ would mean the increment of intrinsic energy for a unit increment in volume, *the temperature remaining constant.*

We have every evidence in favor of the hypothesis that heat is a mode of motion of the molecules of a body. Its temperature is due to the kinetic energy of this motion; hence $\frac{\partial U}{\partial T} dT$ denotes the increment of the kinetic part of the intrinsic energy. The other part of the increment of the internal energy, namely, $\frac{\partial U}{\partial v} dv$, will be work done against the forces between these molecules. These forces will depend on the distances of the molecules from each other, and therefore on the volume of the body. The work done against these forces, (when the temperature, and consequently the kinetic energy of the body, remains constant), will therefore appear as potential energy. Whenever there are no internal forces between the molecules, the term $\frac{\partial U}{\partial v} dv$ will be zero. That is, the intrinsic energy of the body will be independent of the volume.

If such a body expands without doing work against external pressure, its temperature will remain constant, if no heat is communicated from without. For, from the equation

$$dQ = \frac{\partial U}{\partial T} dT + p\,dv,$$

we see that when $dQ = 0$, there being no heat communicated from without, and $p\,dv = 0$, there being no external work done, then

$$\frac{\partial U}{\partial T} dT = 0.$$ That is, $dT = 0$, since $\frac{\partial U}{\partial T}$ cannot $= 0$.

Vice versâ, if when the body expands without doing external work, and without receiving heat from without, its temperature remains constant, then

$$\frac{\partial U}{\partial v}dv = 0. \quad \text{Hence} \quad \frac{\partial U}{\partial v} = 0.$$

That is to say, *the intrinsic energy of such a body will be independent of its volume.*

Gay-Lussac's experiments disclosd such a behavior on the part of perfect gases. These experiments were verified later by Joule and Regnault. We conclude, therefore, that for erfect gases the first law of thermodynamics will have the following form:

$$dQ = \frac{\partial U}{\partial T}dT + pdv.$$

A perfect gas may be described as a body which, when expanding without doing external work, will neither cool nor heat.

THE VARIOUS MATHEMATICAL FORMS OF STATEMENT OF THE FIRST LAW FOR PERFECT GASES.

The rate $\frac{\partial U}{\partial T}$ has a definite name in thermodynamics. Suppose that the quantity of gas under consideration is one unit weight, i.e., one kilogramme; $\frac{\partial U}{\partial T}$ means then the quantity of heat, measured in mechanical units, which we would have to communicate to one unit weight of the gas at constant volume,

in order to raise its temperature by one degree, if the rate at which heat is supplied during a rise of temperature were constant. This quantity of heat is called the *specific heat of the gas at constant volume*, and is denoted by C_v. Now since $p = \dfrac{RT}{v}$ and $\dfrac{\partial U}{\partial T} = C_v$, we can write down the first law of thermodynamics for perfect gases as follows:

$$dQ = C_v dT + \frac{RT}{v}dv. \quad \ldots \quad \ldots \quad \textbf{(1)}$$

From equation (1) we can eliminate v or T by means of the relation $pv = RT$, and obtain

$$dQ = (C_v + R)dT - \frac{RT}{p}dp \quad \ldots \quad \ldots \quad \textbf{(2)}$$

and

$$dQ = \frac{C_v}{R}vdp + \frac{C_v + R}{R}pdv. \quad \ldots \quad \ldots \quad \textbf{(3)}$$

Equations (1), (2), (3) represent three ways of stating mathematically the first law of thermodynamics in the case of a perfect gas. They differ from each other only in the selection of the co-ordinates.

These expressions contain two physical constants of the gas, viz., $C_v =$ specific heat at constant volume, and R. Both these constants must, of course, be determined experimentally. The quantity C_v being difficult to determine experimentally, it is preferred to put these formulæ into a different form, containing $C_p =$ specific heat at constant pressure.

To bring out the meaning of this physical constant, and show its relation to C_v, suppose that we have a unit weight of air enclosed in a cylinder by means of a piston, which can glide up and down the cylinder without friction. Its temperature, volume, and pressure being T, v, and p, we must have $pv = RT$. Clamp the piston, and apply heat to the gas until its temperature rises by dT. Let dQ_1 be the mechanical measure of this heat communicated to the gas during this operation; then

$$dQ_1 = \frac{\partial U}{\partial T}dT = C_v \, dT.$$

Now loosen the clamp, the volume will increase, since the temperature is now $T + dT$. During this second operation communicate heat to the expanding gas so as to keep its temperature constant.

The volume will expand from v to $v + \frac{\partial v}{\partial T}dT$, overcoming pressure p. Observe that $\frac{\partial v}{\partial T}$ represents the rate of variation of volume due to variation of temperature, the pressure being constant. Hence from $pv = RT$ we obtain

$$\frac{\partial v}{\partial T} = \frac{R}{p}.$$

Let dQ_2 be the heat communicated during this second operation; then

$$dQ_2 = p \, \frac{\partial v}{\partial T}dT = RdT.$$

$$dQ_1 + dQ_2 = (C_v + R)dT.$$

At the end of these two operations we have a change in temperature $= dT$, a change in volume $= \dfrac{\partial v}{\partial T}dT$, and external work equal to $p\dfrac{\partial v}{\partial T}dT$.

Consider now another process, by means of which the same change in temperature, the same change in volume, and the same external work is produced. Let us call the rate at which heat must be applied to the unit weight of the gas, when it expands at constant pressure, C_p. Apply heat until the same change in volume is produced as before; the final temperature will be $T + dT$, as before. The pressure in the second case being the same as in the first, we shall have the same external work done during the expansion, and the increment in internal energy will also be the same, since the change of temperature is the same; hence the quantity of heat communicated will also be the same. Call it dQ; then

$$dQ = C_p dT.$$

But since $dQ = dQ_1 + dQ_2$, we must also have

$$C_p = C_v + R \quad \text{or} \quad C_v = C_p - R.$$

Substituting in equations (1), (2), (3), we obtain

$$dQ = (C_p - R)dT + \frac{RT}{v}dv ; \quad \cdot \quad \cdot \quad \cdot \quad (1^a)$$

$$dQ = C_p dT - \frac{RT}{p}dp ; \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (2^a)$$

$$dQ = \frac{C_p - R}{R}vdp + \frac{C_p}{R}pdv. \quad \cdot \quad \cdot \quad \cdot \quad (3^a)$$

The Ratio of Specific Heats.

We will now introduce a new constant, namely, $\frac{C_p}{C_v} = k$. This physical constant of a gas was first introduced by Regnault, and is of vital importance, for the reason that k can be determined experimentally with great accuracy by determining the velocity of sound through the gas.

Regnault found k for air $= 1.41$.

C_p we can also determine by experiment; hence we can calculate R.

Vice versá, if R and C_p are determined experimentally, then both C_v and k can be calculated.

The relation $C_p = R - C_v$, as it stands, applies to values of these physical constants measured in mechanical units. Dividing by J—the mechanical equivalent of heat—we obtain

$$\frac{C_p}{J} = \frac{R}{J} - \frac{C_v}{J},$$

or

$$c_p = \frac{R}{J} - c_v,$$

where c_p and c_v are measured in kg. calories.

Calculation of the Mechanical Equivalent of Heat.

An interesting relation is obtained from the last equation. Remembering, namely, that $\frac{C_p}{C_v} = k$, we obtain $J = \frac{Rk}{(k-1)c_p}$.

This is the relation first pointed out by Robert Mayer, and actually employed by him to calculate J.

Before we can apply it to any gas, we must find the value of R. Let us find the same for air.

$$R = \frac{p_0 v_0}{273}.$$

Regnault found that at the barometric pressure of 760 mm. the value for v_0 of one unit weight of air is .7733 cubic meters. But since our units are kilogrammes and meters, we have to change the above value of p accordingly.

The specific weight of mercury used by Regnault is 13.596; we get therefore

$$p_0 = 100^{\square dm} \times 7.6^{dm} \times 13.596 = 10333 \text{ kg. per square meter.}$$

Hence, since $v_0 = .7733$ cubic meter,

$$R = \frac{10333 \times .7733}{273} = 29.27.$$

The values of k and c_p for air were determined by Regnault. They are $k = 1.41$, $c_p = .2375$. Hence we obtain

$$J = \frac{29.27 \times 1.41}{.41 \times .2375} = 423.8 \text{ kg.-meters.}$$

The value of J obtained by direct experiments is very nearly 424. So much for the physical constants of a perfect gas.

A table of c_v and c_p for various gases will be given presently.

To sum up: The mathematical statement of the first law of thermodynamics in the case of perfect gases expresses a quantitative relation between the increments in volume, pressure, and temperature of a gas when a small quantity of heat dQ is added to or taken away from it. This relation contains the physical constants R, C_p, C_v, k, which must be determined by experiment. *Experiment tells us that C_p, just like R, is independent of pressure and temperature. Hence C_v and k are also independent of these.* This makes the thermodynamic study of the behavior of perfect gases comparatively easy.

It is well now to consider how we can apply the first law of thermodynamics to the solution of a few simple problems.

Problems.

We shall consider two problems in particular:

(1) We shall determine the amount of heat absorbed by a gas when it expands under constant pressure.

(2) We shall determine the amount of heat absorbed by a gas when it expands at constant temperature.

To solve these equations we must observe that a proper selection among the three mathematical statements of the first law of thermodynamics will afford us considerable mathematical advantage.

For the first problem we select one of the formulæ, containing v and p as independent variables, and since p in this

case is to be constant, the term containing dp becomes zero. Hence

$$dQ = \frac{C_p - R}{R} v\,dp + \frac{C_p}{R} p\,dv$$

becomes

$$dQ = \frac{C_p}{R} p\,dv.$$

Integrating from $v = v_1$ to $v = v_2$, we get

$$Q = \int dQ = \frac{C_p}{R} p \int_{v_1}^{v_2} dv = \frac{C_p}{R} p(v_2 - v_1).$$

Numerical Example.—Consider a kilogramme of air at barometric pressure of 760 mm.; that is, let the initial pressure be 10333 kilog. per square meter, let the initial volume be .7733 cubic meter, and let $v_2 = 2v_1$.

Since $c_p = .2375$ kg. calories, and $C_p = .2375 \times 424$, therefore the amount of heat absorbed by the gas while expanding under constant pressure from v_1 to $2v_1$ will be

$$Q = \frac{10333 \times .2375 \times 424}{29.27} \times .7733 = 27490 \text{ kg. meters}$$

$$= \frac{27490}{424} \text{ kg. cal.}$$

In the second problem, where we wish to determine the amount of heat that must be supplied to the gas in order to expand it under constant temperature, we take the formula (1^a)

$$dQ = (C_p - R)dT + \frac{RT}{v} dv,$$

because there dT being zero, when T is constant, we obtain

$$dQ = \frac{RT}{v}dv, \quad \text{and hence} \quad Q = RT\int_{v_1}^{v_2}\frac{dv}{v} = RT\log\frac{v_2}{v_1},$$

which is the total amount of heat measured in kg. meters which is absorbed by the gas while expanding isothermally from volume v_1 to volume v_2. To determine the total amount of work done, we put

$$W = \int_{v_1}^{v_2}pdv = RT\int_{v_1}^{v_2}\frac{dv}{v} = RT\log\frac{v_2}{v_1}.$$

This result, compared with the preceding one, gives an identity. *It tells us that the entire amount of heat put into the gas was utilized to do external work ; for since the temperature remains constant, none of the heat supplied goes to increase the intrinsic energy of the gas.*

Isothermal and Adiabatic Curves.

If we make the supposition that during the expansion of the gas the temperature remains constant, we have from Mariotte–Gay-Lussac's law $pv = C$.

Represent this result graphically, taking p for ordinates and v for abscissæ. The resulting curve is an equilateral hyperbola referred to its asymptotes. *Such a curve is called an isothermal curve.* (Fig. 1.)

There is evidently an isothermal curve for every temperature; hence an infinite number of them, but every one of them is an equilateral hyperbola in the case of a perfect gas.

The isothermal curves of a perfect gas form a system of curves which never intersect. For suppose there is a point where two curves do intersect, this would have to be a point where at different temperatures the pressure is the same for the same volume,—which is absurd.

FIG. 1.   FIG. 2.

Let us suppose again that we diminish the pressure without introducing additional heat. The piston will go up, hence the temperature will diminish; and as soon as a point is reached where $p_1 v_1 = R T_1$ the expansion will cease.

If we *plot a curve expressing a relation between p and v at any moment during this expansion, we get what is called* AN ADIABATIC or ISENTROPIC CURVE. (Fig. 2.)

The equation of this curve will be deduced presently.

Equation of the Adiabatic Curve of a Perfect Gas.

Since no heat is communicated during an adiabatic expansion, the following relation must exist at any moment between the physical constants of the gas:

$$0 = (C_p - R)dT + \frac{RT}{v}dv.$$

$$\therefore (R - C_p) \log \frac{T_2}{T_1} = R \log \frac{v_2}{v_1},$$

or

$$\frac{T_2}{T_1} = \left(\frac{v_2}{v_1}\right)^{\frac{R}{R - C_p}} = \left(\frac{v_2}{v_1}\right)^{\frac{C_p - C_v}{- C_v}} = \left(\frac{v_2}{v_1}\right)^{1 - k} = \left(\frac{v_1}{v_2}\right)^{k - 1}.$$

Let us illustrate this by an example.

Suppose the initial temperature is 0° C. above the freezing-point, and a certain initial volume of a kg. of air is compressed to $\frac{1}{2}$ the volume; calculate the rise in temperature.

$$T_1 = 273, \qquad \frac{v_1}{v_2} = 2.$$

$$\therefore \frac{T_2}{273} = (2)^{.41} = 1.329, \quad \text{or} \quad T_2 = 363° \text{ C.}$$

Hence $t_2 = T_2 - 273 = 90°$ C. above the freezing-point.

Compressing the initial volume to $\frac{1}{4}$, we find

$$t = 209° \text{ C.}$$

Compressing the initial volume to $\frac{1}{10}$, we find

$$t = 429° \text{ C.}$$

We shall now calculate the external work done, when the gas expands adiabatically.

From $pv = RT$ we get

$$p_1 v_1 = RT_1, \qquad p_2 v_2 = RT_2.$$

$$\therefore \frac{T_2}{T_1} = \frac{p_2 v_2}{p_1 v_1}. \qquad \text{But we found} \qquad \frac{T_2}{T_1} = \left(\frac{v_1}{v_2}\right)^{k - 1}.$$

Hence $\quad \dfrac{p_2}{p_1} = \left(\dfrac{v_1}{v_2}\right)^{k}, \quad$ or, more generally, $\quad p = \dfrac{p_1 v_1{}^{k}}{v^{k}}.$

The last equation is the equation of an adiabatic of a perfect gas. It is evidently of the form

$$y = \frac{\text{const.}}{x^k}.$$

To calculate the external work done during an adiabatic expansion from volume v_1 to v_2, we have

$$W = \int_{v_1}^{v_2} p\,dv = p_1 v_1^k \int_{v_1}^{v_2} \frac{dv}{v^k} = \frac{p_1 v_1^k}{k-1}\left\{ \frac{1}{v_1^{k-1}} - \frac{1}{v_2^{k-1}} \right\}$$

$$= \frac{R}{k-1}(T_1 - T_2).$$

A family of adiabatic curves never intersect each other, but every adiabatic curve intersects every isothermal curve.

The axes of p and v are asymptotes to the adiabatics of a perfect gas, but the adiabatic passing through a given point is more steeply inclined to the p axis than the isothermal passing through the same point.

Summary.

It has been shown so far that heat is a form of energy, and that therefore it obeys the Principle of Conservation of Energy. The constant ratio at which it is convertible into mechanical energy is 424; that is to say, if the quantity of heat which must be supplied to the unit mass of the standard substance (one cubic decimeter of pure distilled water at 4° C. and 760 mm. barometric pressure) in order to raise its temperature 1° C. be called a unit of heat, then this unit of heat is equivalent to 424 mechanical units of work, the weight of the unit mass at

a definite place, that is, the kilogramme weight, being taken as the unit of force and the meter as the unit of length. Briefly stated, the mechanical equivalent of a kilogramme calorie is 424 kilogramme-meters. After that it was shown that if we add a quantity of heat to a body that heat will appear partly as an increment of the intrinsic energy of the body and partly as external work. For very small quantities of heat this can be stated as follows :

$$dQ = dU_1 + dU_2 + dW,$$

which is the most general form of the First Law of Thermodynamics. In this equation dU_1 is the increment of the intrinsic energy due to increase of the sensible heat of the body, and dU_2 is the increment of the intrinsic energy due to the increment of internal potential energy of the body. The external work dW was shown then to be pdv, as long as we limit ourselves to a particular kind of external work, that is, work done by the body in expanding against a uniform, normal surface pressure.

Limiting ourselves to such physical processes in which the state of the body, which is the seat of these processes, can be described completely at any moment by temperature, volume, and pressure, it was shown that the first law of thermodynamics can be stated as follows:

$$dQ = \frac{\partial U}{\partial t}\, dt + \left(\frac{\partial U}{\partial v} + p\right)dv.$$

The application of the first law of thermodynamics to the study of such physical processes in various classes of physical

bodies was then in order. We commenced with the simplest class of physical bodies, that is, with perfect gases. Starting with the Boyle and the Mariotte–Gay-Lussac Laws, and remembering that the intrinsic energy of a perfect gas is independent of its volume, we showed that the First Law of Thermodynamics for perfect gases can be stated as follows :

$$dQ = C_v \, dT + p \, dv,$$

when C_v is the specific heat of the gas at constant volume, measured in mechanical units. By the relations $C_p = C_v + R$ and $pv = RT$ we then gave the various forms of statement of the above equation, these various statements differing from each other in the selection of the independent variables p, v, and T, and the physical constants C_p, C_v, R, and k. An important observation was then made, and that was, that according to Regnault's experiments, C_p and therefore C_v, R, and k, are the same for all temperatures, volumes, and pressures at which the gases retain their characteristic properties of a perfect gas.

The application of these various forms of statement of the First Law of Thermodynamics for perfect gases was then made, and the isothermal and adiabatic changes of such gases discussed. We ended with the discussion of isothermal and adiabatic or isentropic curves of a perfect gas.

We could, following the same method of discussion, apply now the first law of Thermodynamics to the study of physical processes of above description in the case of any other class of physical bodies. It is evident, however, that since the fundamental relation between pressure, volume, and temperature

in the case of physical bodies in general is far from being as simple as in the case of perfect gases,—it is evident, we say, that our discussion would lead to very complicated equations, involving physical constants which, in very many cases, have not as yet been determined experimentally. We shall therefore abstain from a general discussion, but pass on to the application of the first law of thermodynamics, to the study of reversible processes in vapors. This class of bodies is extremely important, particularly from an engineering standpoint, because it is the action of heat upon these bodies that is generally employed as a means of transforming heat energy into mechanical energy, and *vice versá.*

Before making this next step, it is advisable to deduce another general law, which, like the first law of thermodynamics, underlies all reversible heat processes in nature. It is called the Second Law of Thermodynamics.

We close now this part of our course with a discussion of the various methods of expressing the specific heats of gases, and the relations which exist between them.

On the Various Ways of Expressing the Specific Heats of Perfect Gases.

Consider the relation $c_p = c_v + \dfrac{R}{J}$.

This relation says: Given the spec. heat of a gas at constant pressure, the spec. heat at constant volume can be calculated, if the constant R of the gas, and the mechanical equivalent of heat, are known.

We mentioned previously that we could determine the

ratio of the spec. heats by means of the velocity of sound. This gives another method of calculating c_v when c_p is known. But it is very difficult in some gases to determine (k) by velocity measurements. In such cases we must take our recourse to the above formula.

R can be calculated from the formula

$$R = \frac{p_0 v_0}{273}.$$

It is possible, nowever, that the gas cannot oe well observed at the freezing temperature; hence we must look for another method of calculating R.

We can write in every case

$$R = \frac{pv}{T}.$$

At the same temperature and pressure we shall have for the same weight of a standard gas, say well-dried air,

$$R' = \frac{pv'}{T}. \quad \text{Hence} \quad R = R'\frac{v}{v'}.$$

The fraction $\dfrac{v}{v'}$ is the reciprocal value of the spec. weight of the gas, that is of its density, the density of air being taken is equal to unity.

Calling this spec. weight, that is, the density, d, we have

$$R = \frac{R'}{d}.$$

By substituting this value of R in the first equation, we get

$$c_v = c_p - \frac{R'}{d} \frac{1}{J}.$$

R' in our case is 29.27.

Example. Calculate c_v for air.

$$d = 1, \quad \text{hence} \quad c_v = .2375 - \frac{29.27}{424} = .1684.$$

$$\frac{c_p}{c_v} = k = \frac{.2375}{.1684} = 1.41.$$

That is to say, to raise the temperature one degree, a kilog. of air requires only about $\frac{1}{6}$ of the heat that a kilog. of standard water does.

The spec. heats denoted by c_p and c_v refer to a unit weight of the gas, and their unit is that quantity of heat which is necessary to raise the temperature of a unit mass of standard water under standard conditions one degree; that is, in other words, the gas is compared calorically by weight, to water. While, as a matter of fact, it is sometimes more convenient to compare in this respect gases with air, by considering equal volumes, i.e., to determine the spec. heat in such a manner, that the amount of heat necessary to raise the unit volume of a gas one degree, is compared with the quantity of heat necessary to raise a unit volume of air through one degree (at the same temperature and pressure).

We can employ that method of comparison for both specific

heats, considering in one case that the gas and the air are heated at constant pressure, and in the other that the gas and air are heated at constant volume.

Let the volume of a unit weight of gas be v.

The amount of heat which a unit volume must get to raise its temperature one degree at constant pressure must therefore be

$$\frac{c_p}{v} = \gamma.$$

Let the volume of a unit weight of air $= v_1$, then the amount of heat necessary to raise a unit volume through one degree under the same conditions will be

$$\frac{c_p{'}}{v'} = \gamma'.$$

The ratio of these quantities evidently gives us γ_p; that is, the quantity of heat necessary to raise the temperature of the unit volume of a gas at constant pressure measured in terms of the heat necessary to raise the temperature of the unit volume of air under the same conditions. Hence

$$\gamma_p = \frac{\gamma}{\gamma'} = \frac{c_p}{c'_p} \frac{v'}{v} = \frac{c_p}{c'_p} d.$$

Similarly,

$$\gamma_v = \frac{c_v}{c_v{'}} d.$$

TABLE OF SPECIFIC HEATS OF GASES.

		Density.	Specific Heat at Const. Pressure.		Specific Heat at Const. Volume.	
			c_p	γ_p	c_v	γ_v
Air...............	—	1.	0.2375	1.	0.1684	1.
Oxygen..........	O_2	1.1056	0.21751	1.013	0.1551	1.018
Nitrogen..........	N_2	0.9713	0.24380	0.997	0.1727	0.996
Hydrogen...........	H_2	0.0692	3.40900	0.993	2.411	0.990
Chlorine..........	Cl_2	2.4502	0.12099	1.248	0.0928	1.350
Carb. monoxide..	CO	0.9673	0.2450	0.998	0.1736	0.997
Hydroch. acid gas.	HCl	1.2596	0.1852	0.982	0.1304	0.975
Carbonic acid.....	CO_2	1.5201	0.2169	1.39	0.172	1 55
Steam	H_2O	0.6219	0.4805	1.26	0.370	1.36
Ammonia.........	NH_3	0.5894	0.5084	1.26	0.391	1.37
Alcohol....·... ..	C_2H_6O	1.5890	0.4534	3.03	0.410	3.87
Ether.............	$C_4H_{10}O$	2.5573	0 4797	5.16	0.453	6.87

III.

SECOND LAW OF THERMODYNAMICS.

Carnot's Reversible Engine and Carnot's Cycle.

Let us start with a process of expansion and compression of a perfect gas enclosed in a cylinder which is impermeable to heat. The piston which shuts the gas in, can glide up and down without friction. The piston being under a given pressure, the gas will at a given temperature occupy a definite volume. Heat can be communicated to the gas through plug p. Let the length oe on the abscissa denote the original volume v_1 of a gas, and the ordinate ea the initial pressure p_1. Evidently these two conditions determine the temperature of the gas at that moment. Let the gas expand isother-

mally. To accomplish this imagine it connected to a large reservoir A (Fig. 4) of temperature T_1, the same as that of the gas. By gradually diminishing the pressure and expanding
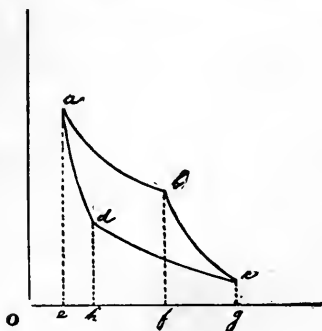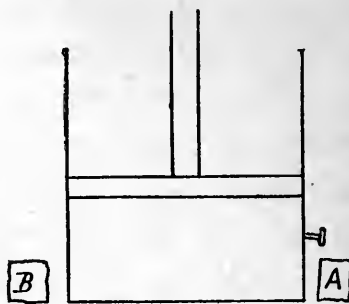

FIG. 3.

FIG. 4.

very slowly, the temperature will remain constant and equal to T_1. Plotting the curve expressing the relation between p and v, we get a part of an isothermal curve. Point b indicates the volume and pressure at the end of the isothermal expansion. Now cut off the heat reservoir A, and let the gas expand slowly still further (by diminishing the pressure), but of course adiabatically, that is to say, the gas expands and decreases in temperature on account of loss of heat due to external work done. The curve of expansion, bc, will be a part of an adiabadic. Call the temperature, when volume v_2 has been reached, T_2. From now on compress the gas, but having first connected the cylinder to a reservoir B of temperature T_2 and of so large a capacity that it will take up all the heat from the compressed gas without changing its temperature perceptibly. The heat generated in the gas by compression will be given off to B, hence the compression will be isothermal. The curve of compression will again be

a part of an isothermal. At this point we impose a *particular condition,* namely, that the gas be compressed until a point is reached where the *isothermal cuts that adiabatic curve which goes through the starting point a.*

Arrived at that particular point, we disconnect the reservoir *B* and continue the compression. From there on the gas is compressed adiabatically, the temperature rises, and when the original temperature T_1 has been reached the gas will evidently have the same volume and will be under the same pressure as at the beginning. *These four operations constitute what is called a Carnot Cycle.*

Now we shall consider the work done by the gas and upon the gas during the various operations in the cycle. The work done during the first expansion can be represented by the area *abfe,* that during the second by *b c g f.*

During the compressions work has been spent upon the gas equal to the areas *cdhg* and *hdae* respectively. The difference between the work done and the work expended is the work gained. This gain must evidently be at the expense of heat given up to the gas by the reservoir *A.*

Heat was taken up from *A* by the gas during the first operation; let us call that Q_1, and during the isothermal compression heat was given out from the gas to the reservoir *B*; let us call that Q_2. Since on the whole a certain quantity *Q* was transformed into work represented by the area *abcd,* it is evident that

$$Q_1 = Q_2 + Q.$$

Let us illustrate that method by an example.

Say that we have .5 kilogr. of air, and an initial pressure of 10 atmospheres, that is equal to 7600 mm. barometric pressure or 103,330 kilogr. per square meter.

Let the initial volume be $\frac{1}{10}$ cubic m.

$$v_1 = .1 \text{ cm.}$$

$$p_1 = 103,330 \text{ klg. per sq. m.}$$

$$\text{Weight} = .5 \text{ kg.}$$

$$2p_1v_1 = RT_1.$$

$$\therefore T_1 = \frac{103330 \times .1 \times 2}{29.27} = 706°.$$

Suppose now that we work between the reservoirs A and B at 706° and 293° respectively.   Hence

$$T_1 = 706°, \qquad T_2 = 293°.$$

We will proceed by allowing the gas to expand isothermally, until the volume is equal to v_2, and suppose for convenience of calculation

$$\frac{v_2}{v_1} = e = 2.72.$$

Work done by the gas during this expansion $= \displaystyle\int_{v_1}^{v_2} pdv = W_1.$

But in isothermal expansion $pv = RT_1 = $ constant.

$$\therefore W_1 = RT_1 \int_{v_1}^{v_2} \frac{dv}{v} = RT_1 \log \frac{v_2}{v_1} = 29.27 \times 706 \text{ kg. meters.}$$

Heat taken up from A will be $= \dfrac{29.27 \times 706}{424}$ kg. calories.

Passing to the second operation we expand the gas from now on adiabatically, until its temperature is 293°. The final volume will be v_3.

Let the work done during this operation be denoted by W_2, then

$$W_2 = \int_{v_2}^{v_3} pdv.$$

But during this operation $p = \dfrac{p_2 v_2}{v^k}$.

$$\therefore W_2 = \frac{RT_1}{k-1} \left\{ 1 - \left(\frac{v_2}{v_3}\right)^{k-1} \right\} = \frac{R}{k-1} \left\{ T_1 - T_2 \right\}$$

$$= 29,480 \text{ kg. meters.}$$

Compress now isothermally until the point is reached where the isothermal cuts the adiabatic which passes through the starting point $p_1 v_1$ and denote this work of compression by W_3. Then if v_4 be the final volume,

$$W_3 = RT_2 \log \frac{v_4}{v_3}.$$

But since $\left(\dfrac{v_4}{v_1}\right)^{k-1} = \dfrac{T_1}{T_2}$, also $\left(\dfrac{v_3}{v_2}\right)^{k-1} = \dfrac{T_1}{T_2}$, it follows that

$\dfrac{v_4}{v_1} = \dfrac{v_3}{v_2}$ or $\dfrac{v_4}{v_3} = \dfrac{v_1}{v_2}$; $\therefore \log \dfrac{v_4}{v_3} = -\log \dfrac{v_2}{v_1}$; $\therefore W_3 = -RT_2 \log \dfrac{v_2}{v_1}$.

Similarly the work done during the last adiabatic compression will be

$$W_4 = -\frac{R}{k-1}(T_1 - T_2) = -W_2.$$

The total external work represented by the area *abcd* is

$$W = W_1 + W_2 + W_3 + W_4$$

$$= W_1 + W_3$$

$$= R \log \frac{v_2}{v_1}(T_1 - T_2).$$

$$\text{Efficiency} \quad = \frac{W}{W_1}$$

$$= \frac{T_1 - T_2}{T_1}.$$

This relation expresses the *second law of thermodynamics,* but only *in a very limited form ;* that is to say, this relation being simply a mathematical expression for the efficiency of a particular machine, Carnot's engine, operating in a perfectly definite manner,—that is, by simple reversible cycles, upon a particular class of bodies, namely, perfect gases,—this relation should not be considered to be anything more than it really is

namely, a law which holds true for a particular class of physical processes taking place in a particular class of physical bodies.

It was in this form that the great French engineer, Sadi Carnot, first discovered the law, seventy years ago, in 1824. But he did more than that. He also pointed out that it is only a particular form of a more general law, that is to say, a law which holds true for a class of physical processes much larger than the class we have just described. It was by a train of reasoning first suggested by Carnot's great essay, "Réflexions sur la puissance motrice du feu et sur les machines propres à la développer," that subsequent investigators, and foremost among them Clausius and Rankine, were able to extend the above relation into a general law, called the second law of thermodynamics.

Before proceeding any further in our discussion towards the generalization of the above efficiency relation into the second law of thermodynamics let us first examine carefully the foundation on which this relation rests.

Consider each one of the four operations which taken together constitute Carnot's cycle. Any one of them when reversed will produce just the opposite effect. Take for instance the second operation, that is, the first adiabatic expansion. If at the completion of this operation we reverse the operation, we can bring the gas back into the state which it had at the beginning of this operation. The reversed operation will cost us mechanical work of compression equal to the area $bcgh$. That work will appear as intrinsic energy in the gas, that is, as heat, in consequence of which the temperature of the gas is increased from T_2 to T_1. If the first operation be

called the direct and the second the reversed, then we can say that the direct and the reversed operation just neutralize each other. The same is true of every other operation of the cycle. It follows, therefore, that the whole cycle can be reversed and the reversed cycle will produce just the opposite effect of the direct cycle, that is to say, it will deprive the reservoir B of Q_2 units and add Q_1 units of heat to reservoir A, and it will also transform $Q_1 - Q_2 = Q$ units of work into heat. In the first cycle heat passes from a hot body to a cold body, but some of this heat in its journey to the cold body is transformed into mechanical work and therefore never reaches the cold body. In the reversed cycle mechanical work is expended, in order to transfer Q_2 units of heat from the cold body to the hot, and in addition generate Q units of heat which are also given up to the hot body.

Such a cycle is called a reversible cycle. The relation

$$\frac{Q}{Q_1} = \frac{T_1 - T_2}{T_1}$$

is evidently the same no matter whether the cycle be taken in the direct or in the reversed sense.

Suppose now that during any one of the operations the gas had changed chemically, but in such a way that its chemical constitution could not be restored by reversing the operation. Such an operation would not be reversible, nor would the cycle of which this operation forms a component part be reversible. In such a cycle the above relation may or may not be true. A special investigation is required to clear up this point; but since we are not going to discuss it in our course it is well that you should be told that it is not true.

It should also be observed that there are a great many reversible cyclic processes in all branches of physical sciences which do not apparently resemble Carnot's cycles of operations. A great many illustrations may be cited from chemistry, electricity and magnetism, etc. Whether in these Carnot's law of efficiency or the general form of it which we are about to deduce is applicable or not, must be decided by investigations which are outside of the limits of our course. What we propose to do is simply this : we are going to prove the applicability of Carnot's law of efficiency, and therefore of all its extensions, to all physical processes which consist of operations any one of which can be performed reversibly by a Carnot engine.

The first step in our work will be to prove that the efficiency of a Carnot cycle depends on the temperatures of the reservoirs A and B as expressed above, no matter what the substance may be upon which we operate. To do this we shall start from an axiom first stated by Clausius, and therefore called the

Axiom of Clausius.

Heat cannot pass from a cold body to a hot body of itself.

This statement includes, that by conduction of heat, or by concentration, reflection, etc., of radiant heat, no heat can be transferred to a body at the expense of a colder one, unless the process of transference involves the expenditure of some sort of energy.

In the preceding discussion we saw that heat passed from a cold to a hot reservoir, but not without expenditure of work.

So we might say, instead of "of itself," "without work or compensation."

The truth of this axiom is proved in the same way as the truth of Newton's axioms of motion, that is, by an appeal to experience.

We shall now prove that the ratio between the heat transformed into work by a simple reversible cycle and the heat transferred from a hot body to a colder body during the same cycle is independent of the material which we employ in the cylinder of our ideal engine, and that it can depend only on the temperatures of the reservoirs A and B.

For this purpose we employ two equal cylinders A and B containing two different substances, upon which we propose to perform simple reversible cycles. *Each cycle is performed between the same two reservoirs,* so that the temperatures between which we operate are the same for each cycle. Perform now cycle I with the cylinder A, and suppose that a quantity of heat equal to Q is transformed into mechanical work, and that a quantity of heat equal to Q_2 is transferred to the colder reservoir. Pass now to the other cylinder and perform a similar cycle, but in such a way that again a quantity Q of heat is transformed into mechanical work. A certain quantity of heat, say Q_2', will be transferred to the colder reservoir. We wish to prove now that $Q_2' = Q_2$. For if it is not, suppose that $Q_2' > Q_2$. After performing cycle I in the direct order, by which a quantity of heat Q is transformed into mechanical work and Q_2 transferred to the colder reservoir, employ cylinder B to perform cycle II in the reverse order, so that the mechanical work obtained by cycle I is retransformed into heat, and a quantity of heat equal to Q_2' is trans-

ferred from the cold to the hot reservoir. At the end of the two cycles the only change that still remains is the transfer of a quantity of heat equal to $Q_2' - Q_2$ from the cold to the hot reservoir, that is, a transference of heat from a body of lower to a body of higher temperature without any compensation. This is contrary to the axiom of Clausius, hence the supposition that $Q_2' > Q_2$ must be dismissed.

Next suppose that $Q_2' < Q_2$. We can prove that this supposition also violates our axiom by going through cycle II in the direct and cycle I in the reverse order.

Hence Clausius' Axiom leads to the conclusion that $Q_2' = Q_2$. That is to say, *whenever mechanical work is obtained at the expense of heat by a reversible cyclic operation, heat is transferred from a hot to a cold body and the ratio of the work obtained to the quantity of heat transferred from the hot to the cold body is independent of the substance which is operated upon.*

That ratio will therefore be the same for a perfect gas as for any other substance. We proceed to calculate it for a perfect gas. Let the temperatures of the two reservoirs be T_1 and T_2 and suppose that $T_1 > T_2$.

We found previously that in the case of a perfect gas

$$\frac{Q}{Q_1} = \frac{T_1 - T_2}{T_1},$$

or

$$\frac{Q_1}{Q} = \frac{Q + Q_2}{Q} = 1 + \frac{Q_2}{Q} = \frac{T_1}{T_1 - T_2},$$

$$\therefore \quad \frac{Q_2}{Q} = \frac{T_1}{T_1 - T_2} - 1 = \frac{T_2}{T_1 - T_2}.$$

We see therefore that this ratio in the case of a perfect gas and therefore also in the case of any other substance depends on the two temperatures between which the cycle is performed.

A slight modification of this relation will give us another form of stating the second law of thermodynamics applicable to simple reversible cycles. From this relation we obtain

$$\frac{Q_2}{T_2} = \frac{Q}{T_1 - T_2}.$$

We obtained previously

$$\frac{Q_1}{Q} = \frac{T_1}{T_1 - T_2};$$

hence

$$\frac{Q_1}{T_1} = \frac{Q}{T_1 - T_2}.$$

Combining this with the above we obtain

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2}, \quad \text{or} \quad \frac{Q_1}{T_1} - \frac{Q_2}{T_2} = 0, \quad \text{or} \quad \frac{Q_1}{T_1} + \frac{-Q_2}{T_2} = 0.$$

$- Q_2$ is the heat *given off to the cold reservoir by the substance* operated upon, hence $- (- Q_2)$ or $+ Q_2$ can be said to be the heat *received by the substance from the cold reservoir*. With that mental reservation we can write down

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0.$$

This is the more compact and at the same time more flexible form of stating the second law of thermodynamics applicable to simple reversible cycles. The English translation of this mathematical statement is : *If in a simple reversible cycle the heats received by the substance operated upon be divided by the temperatures at which these heats were received and the quotients thus obtained be added together, then will the sum be equal to zero.*

This statement of the second law of a simple reversible cycle is certainly not nearly as clear nor physically as intelligible as the other statement, which involved the efficiency of an ideal reversible engine, but, as will be presently seen, it enables us to extend in a very simple manner the applicability of this law to *complex reversible cycles* and thus give the second law of thermodynamics a much more general form.

General Form of the Second Law of Thermodynamics.

Complex Cycles.

So far we have considered cycles between two temperatures only. We now proceed to extend this to a so-called *complex cycle,* that is, a cycle of operations between several reservoirs of different temperatures. We commence with three reservoirs of temperature T_1, T_2, and T_3.

Let *ab* (Fig. 5) denote an isothermal expansion at the temperature T_1, *bc* an adiabatic expansion down to the temperature T_2, *cd* an isothermal expansion at the temperature T_2, *de* an adiabatic expansion down to the temperature T_3, *ef* an *isothermal compression* at the temperature T_3, the isothermal

compression to continue until the isothermal curve *ef* cuts the adiabatic through *a,* and lastly *fa* an adiabatic compression to the starting point.

During the expansions *ab* and *cd* the substance operated upon takes up the quantities of heat Q_1, Q_2 from the reservoirs A and B at temperatures T_1 and T_2, and during the
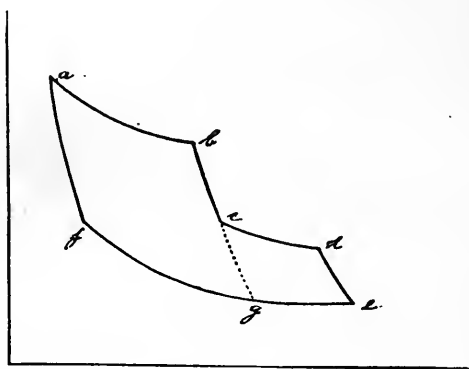

Fɪɢ. 5.

isothermal compression *ef* it takes up the negative quantity of heat $- Q_3$ from the reservoir C at temperature T_3. The external work done during the cycle is represented by the area *abcdefa.*

We proceed to show now that a similar relation holds true in this case as in the simple cycle.

To do that, let us produce the adiabatic *bc* until it cuts the isothermal *fe* at *g*; then will the whole complex cycle be divided into two simple cycles *abgfa* and *cdegc.*

The negative quantity Q_3 consists of q_3 and q_3', given off to the coldest reservoir during the isothermal compressions *gf* and *eg* respectively. We can now write down the symbolical

statement of the second law for each one of these two simple cycles, viz. :

$$\frac{Q_1}{T_1} + \frac{q_3}{T_3} = 0 \text{ for cycle } abcgfa;$$

$$\frac{Q_2}{T_2} + \frac{q_3'}{T_3} = 0 \text{ `` `` } cdegc.$$

Adding these two we obtain

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} + \frac{q_3 + q_3'}{T_3} = 0;$$

or, since $q_3 + q_3' = Q_3$,

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} + \frac{Q_3}{T_3} = 0.$$

In the same manner we can prove this relation for a complex cycle divisible into any number of simple cycles and obtain

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} + \frac{Q_3}{T_3} + \ldots + \frac{Q_n}{T_n} = 0, \text{ or } \sum_1^n \frac{Q}{T} = 0.$$

If the cycle be of infinite complexity, that is to say, if it be representable by an infinite number of infinitely small elements of adiabatic and isothermal curves, it is evident that the relation $\sum \frac{Q}{T} = 0$ will still hold true. Of course each one of

the Q's will be infinitely small and the sum will be an infinite sum. We can therefore express this relation in the notation of the infinitesimal calculus, thus:

$$\int \frac{dQ}{T} = 0.$$

A reversible cycle of this complexity will evidently in the limit be representable by a continuous closed curve. The area bounded by this curve will represent the external work done during the cycle if the cycle be performed in the direct sense, otherwise it will represent the external work spent in order to transfer a certain amount of heat to the hot reservoir, a part of which comes from the cold reservoir.

The statement of the second law of thermodynamics (applicable to reversible cycles) as given by the last equation, though very general, gives us but little information about the various elements of which the cycle is composed. It gives us no information about the progress of the various physical processes which taken together constitute the cycle. It has the defect which is common to all integral laws. For such laws give us the total effect of a series of physical processes without giving us the separate effect of each process of the series. Take for instance the integral laws of Keppler which describe the motion of the planets around the sun. They tell us all about the areas traced out by radii vectores of the planets during a finite time, about the periodic times, and about the orbits of the planets, but they do not tell us anything about the action which is going on at any and every moment between the sun

and the planets to produce these integral effects. It took no less a genius than that of a Newton to infer these differential effects from the integral effects discovered by Keppler. The inference was the law of gravitation. To draw that inference Newton had to invent the infinitesimal calculus. We may well assert that he had to invent it ; for a simple consideration will convince you that the process of passing from an integral physical law to the differential law—that is, the law which describes a physical process as it progresses from point to point through infinitely small intervals of space and time—is exactly the same as the mathematical process of passing from an integral to the differential of that integral.

We are now ready to discuss the differential of the integral

$$\int \frac{dQ}{T} = 0.$$

Consider any one of the infinitely small terms $\frac{dQ_{12}}{T_{12}}$ in the
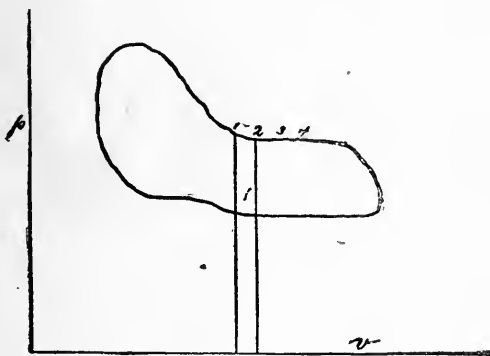

FIG. 6.

infinite series $\int \frac{dQ}{T}$. The subscripts 12 (Fig. 6) denote that dQ_{12} is the heat taken up during the infinitely small element

12 of the cycle and that T_{12} was the mean temperature of the substance operated upon at that particular moment. It is evident that dQ_{12} depends on the instantaneous state of the substance operated upon at that moment, and also upon the nature of the operation represented by the element 12. In other words, dQ_{12} depends on the volume, pressure, and temperature, and the method of their variation during the operation represented by the element 12. Now all these things are completely defined by the co-ordinates of the extremities of the element, *hence dQ_{12} is a function of these co-ordinates.* The same is true of the infinitely small quantity $\dfrac{dQ_{12}}{T_{12}}$.

Consider now a quantity ϕ, and suppose it to be a finite, continuous, and singly-valued function of the pressure, volume, and temperature of the substance operated upon. ϕ will therefore have definite values at every point of any cyclic diagram.

Denote by ϕ_1, ϕ_2, ϕ_3, ... ϕ_n the values of ϕ at the various points 1, 2, 3, ... n all around the cyclic diagram and consider the differences.

$$\phi_2 - \phi_1 = \Delta_1\phi;$$
$$\phi_3 - \phi_2 = \Delta_2\phi;$$
$$\phi_4 - \phi_3 = \Delta_3\phi;$$
$$\cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot$$
$$\cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot$$
$$\phi_n - \phi_{n-1} = \Delta_{n-1}\phi;$$
$$\phi_1 - \phi_n = \Delta_n\phi.$$

It is evident that for every cyclic diagram

$$\Delta_1\phi + \Delta_2\phi + \ldots + \Delta_n\phi = 0.$$

When the points 1, 2, 3, ... n are infinitely near each other, then $\Delta_1\phi$, $\Delta_2\phi$, etc., are infinitely small quantities or what we call in calculus the complete differentials of ϕ at the various points of the curve. We express that by saying that in the limit we shall have the differences $d_1\phi$, $d_2\phi$, $d_3\phi$, etc., but an infinite number of them and their sum, which will still be zero for every cycle, can be expressed in the ordinary way, thus:

$$\int d\phi = 0.$$

This relation will hold true for every function of pressure, volume, and temperature which has definite values at every point of the cyclic diagram and varies continuously from point to point of the diagram. There are evidently an infinite number of such functions.

If that integral is extended not all around the cyclic diagram, but only between two points, say points 1 and α, then we shall have the integral evidently equal to $\phi_\alpha - \phi_1$; that is to say,

$$\int_1^\alpha d\phi = \phi_\alpha - \phi_1.$$

The value of the integral will depend therefore on the position of the initial and final point of integration and not on the shape of the cyclic diagram between the two points.

This relation throws much light upon our integral $\int d\phi = 0$.

For, consider two integrals $\int d\phi$ along a portion AB of a cyclic diagram (Fig. 7); one integral from A to B along one
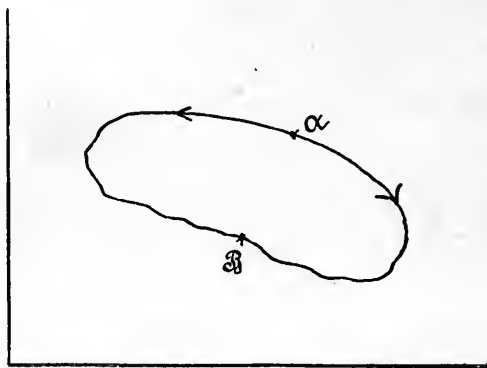
FIG. 7.

part of the diagram in the clockwise direction, and the other along the other part of the diagram in anti-clockwise direction. Denote the first by subscript $(AB)_1$, the second by subscript $(AB)_2$. Then

$$\int_{(AB)_1} d\phi = \phi_B - \phi_A \quad \text{and} \quad \int_{(AB)_2} d\phi = \phi_B - \phi_A.$$

Denote now the integral from B to A along the second part of the cycle by subscript (BA); then evidently

$$\int_{(BA)} d\phi = - \int_{(AB)_2} d\phi = - (\phi_B - \phi_A).$$

It follows therefore that

$$\int_{(AB)_1} d\phi + \int_{(BA)} d\phi = \int_{(AB)_1} d\phi - \int_{(AB)_2} d\phi = (\phi_B - \phi_A) - (\phi_B - \phi_A) = 0,$$

as it should be, since

$$\int_{(AB)_1} d\phi + \int_{(BA)} d\phi = \text{integral all around the cycle.}$$

We can therefore say that the integral all around the cyclic diagram vanishes because the value of the integral between any two points of the diagram depends on the position of the two points and not on the shape of the diagram between these two points. The only other way in which that integral could vanish would be that $d\phi$ is zero for every element of every cycle, in which case ϕ would be a constant. This is contrary to our supposition, for we supposed that it is a variable function of volume, pressure, and temperature.

A careful inspection of the series which in the limit gave the integral $\int d\phi$ will convince you that this integral between any two points of any cyclic diagram depends on the position of these two points and on nothing else, because the quantity under the integral sign is a perfect differential of a function ϕ which is finite, continuous, and singly valued at every point of any cyclic diagram. We conclude, therefore, since the integral $\int \frac{dQ}{T}$ taken around a diagram

representing any reversible cyclic process vanishes, that $\dfrac{dQ}{T}$ is the complete differential of a function S which is a finite, continuous, and singly-valued function of the volume, pressure, and temperature of the substance upon which we operate. We express this by writing

$$\frac{dQ}{T} = dS.$$

This is the most general form of the second law of thermodynamics. This statement of the second law bears about the same relation to the other statement,

$$\int \frac{dQ}{T} = 0,$$

as the Newtonian law of universal gravitation bears to the three laws of Keppler which describe the motion of planets around the sun. It tells us all about the progress of the infinite number of infinitely small processes which, taken together, constitute the whole reversible cyclic process of which the cyclic diagram is a geometrical representation. We shall illustrate this statement by reference to a particular physical process when we come to the discussion of the application of the two laws of thermodynamics to the study of saturated vapors, which we are now ready to take up.

This statement of the second law of thermodynamics of reversible processes was first given by Clausius. The func-

tion S was named by him the *Entropy* of the system. It is impossible to give a general and yet complete definition of the physical meaning of the entropy function, because this meaning will vary considerably with the nature of the process that we may be considering. Hence it can be discussed only in connection with the discussion of each particular process under consideration. It is desirable, however, to illustrate its meaning by considering a few simple processes.

1st. Suppose a body expands reversibly at constant temperature from volume v_1 and pressure p_1 to volume v_2 and pressure p_2. Let the heat that must be supplied to the body be Q, then

$$Q = T(S_2 - S_1);$$

that is, the heat is equal to the absolute temperature multiplied by the increase of the entropy. In the case of a perfect gas that heat is also equal to the external work done by the gas during the expansion, and this work we found to be equal to $RT \log \dfrac{v_2}{v_1}$.

Hence for isothermal expansions of perfect gases we have

$$S_2 - S_1 = R \log \frac{v_2}{v_1}.$$

2d. If the gas expands adiabatically, then, since no heat is supplied during such expansion, we shall have

$$0 = TdS, \quad \text{hence} \quad dS = 0.$$

That is to say, the entropy remains constant. It is on this account that adiabatic expansion is called sometimes an *isentropic expansion,* the word *isentropic* meaning that the entropy remains constant.

IV.

APPLICATION OF THE TWO LAWS OF THERMODYNAMICS TO SATURATED VAPORS.

We are now ready to take up the discussion of the reversible processes in the next simplest class of physical bodies, that is, saturated vapors. Our discussion will be framed after the model of our discourse on the reversible cyclic processes in the case of perfect gases. We shall therefore commence with an appeal to experience for information about the physical properties of saturated vapors. We did the same thing in the case of perfect gases by taking account of the laws of Boyle and Mariotte–Gay-Lussac, and of the experimental researches of Regnault on the specific heats of perfect gases. We shall then put the two laws of thermodynamics into a suitable form by taking proper account of this information about the physical properties of saturated vapors. This will give us two mathematical statements of these laws involving certain physical constants of saturated vapors. Some of these constants are known from experimental researches just as in the case of perfect gases; others we shall have to calculate with the assistance of the two laws. Hence after modelling properly our two fundamental laws,

we shall proceed, just as we did in the case of perfect gases, to calculate and tabulate the various physical constants of saturated vapors. Having done that, we shall then be ready to pass on to the discussion of isothermal and adiabatic expansions of saturated vapors, calculating in each case the external work done and the heat supplied to the expanding vapor. Since water-vapor is the substance most generally employed in our vapor-engines, it is advisable to concentrate our attention as much as possible upon that vapor. The discussion will nevertheless lose very little of its generality, since in dealing with saturated water-vapor we have to consider the same questions that would have to be considered in any other vapor.

Physical Properties of Saturated Vapors.

Consider a cylinder A (Fig. 8) in which a piston B can slide up and down without friction. Let the volume enclosed by
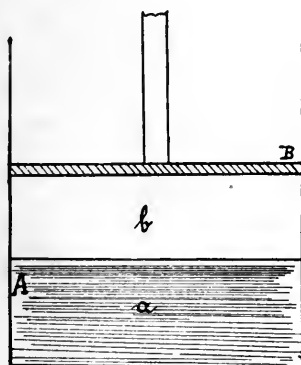

Fig. 8.

the piston be denoted by v, and let a part a of this volume contain a volatile liquid. The other part b will be vapor of

that liquid. Let the temperature be uniform throughout and equal to *T*. Experience tells us that this *vapor, as long as it is in contact with its own liquid, has a definite tension which depends on the nature of the liquid and on its temperature and on nothing else.* Let the pressure on the piston be just such as to be in equilibrium with the tension of the vapor at the temperature *T*. Suppose now that the piston is pushed down through a very small distance ; the volume of the vapor is diminished ; experience tells us that the vapor will condense. *Vice versâ,* if the piston is slightly raised, keeping the temperature constant, then some more liquid will evaporate so as to keep the density in the vapor volume the same as before. We infer, therefore, that *vapor when in contact with its own liquid has the maximum density for that temperature;* in other words, it is *saturated.*

Both the tension and the density of the saturated vapor increase with temperature.

Saturated vapors do not obey the Mariotte–Gay-Lussac law, not even approximately, except for low temperatures. So, for instance, this law cannot be applied to saturated water-vapors at any temperature which is more than only a very few degrees centigrade above the freezing-point.

When a liquid is brought into a space which does not contain the vapor of this liquid, then the liquid will evaporate until its vapor has the maximum density in every part of the surrounding space. The process of evaporation will be slow if the space contains a gas at considerable pressure, but rapid if the space is a vacuum. This is due to the slowness with which the vapor diffuses through a gas of considerable tension. Experience tells us that evaporation is accompanied

by a cooling off of the liquid, and the cooling is the more rapid the quicker the process of evaporation. You are acquainted with the well-known experiment of freezing mercury by bringing it in contact with a volatile liquid which is made to evaporate very rapidly by the action of a pump. If we wish to maintain the temperature of an evaporating liquid constant, then heat must be supplied to it. Conversely, if the saturated vapor be compressed in contact with its own liquid, heat will be developed, and if we wish to keep the temperature constant, then this heat must be taken away. The quantity of heat which is developed by compressing a kilogramme of saturated vapor to liquid at the same temperature and pressure is called the *latent heat of saturated vapor* at that temperature. This is a very important physical constant and has been determined experimentally for a large number of vapors.

When the temperature of a liquid has reached that point at which the tension of its vapor is the same as the pressure of the surrounding space, then the vaporization will be rapid, because it will take place not only on the surface of the liquid, but also in the interior parts, especially if the liquid, as is usually the case, contains small bubbles of a gas, like air, dissolved in it. When this takes place we say that the liquid is boiling. The boiling point of pure distilled water at 760 mm. barometric pressure is 100° C., and it rises with the rise of barometric pressure. The boiling point of water is raised by the solution of foreign substances in it. Sea-water, for instance, has a considerably higher boiling point than pure distilled water at the same barometric pressure. As long as the boiling process continues, the temperature of the liquid re-

mains constant; the heat supplied to the liquid is all utilized to transform the liquid into steam.

If, however, the liquid does not contain any dissolved gases, then the process of boiling is considerably retarded. There is superheating and the boiling is accompanied by the well-known " bumping " or concussive boiling.

When the contact of a saturated vapor with its own liquid is cut off and the vapor allowed to expand slowly, it will cool off, of course, and its density will diminish. The ratio of the diminution of the density to the diminution of temperature is different for different vapors. In some vapors the temperature diminishes more rapidly than the density. Such vapors will condense during adiabatic expansion. If, however, the temperature diminishes more slowly than the density, then the vapor will be superheated, that is to say, it will not remain saturated during adiabatic expansion. In the first case we have superheating and in the second we have condensation during adiabatic compression.

On the Physical Constants of Saturated Vapors.

Let the total weight of the liquid and its saturated vapor in the above-mentioned cylinder be M. Denote by T the absolute temperature of the whole mass, and by v the volume.

Let m = weight of the vapor in kilogrammes;
   p = tension of the saturated vapor in kgr. per sq. m.;
   σ = specific volume of the liquid;
   s =   "   "   "   " vapor.

We shall have then

$$ms + (M - m)\sigma = v,$$

or

$$m(s - \sigma) + M\sigma = v.$$

In what follows we shall write u for $s - \sigma$, hence

$$mu + M\sigma = v.$$

It must be observed, however, that (in the case of water especially) s is large in comparison to σ, so that in most cases we may consider u practically equal to s.

When the temperature T and the weight m of the saturated vapor are given, then the state of the whole mass in the cylinder is completely known. For we know then the pressure and the volume (since the density is completely determined by T), and that is all that we require to know. We can therefore select T and m as our variables.

In order to bring out clearly the meaning of some other physical constants of saturated vapors, we shall consider now two distinct physical processes which we shall call definitional processes.

DEFINITIONAL PROCESS (A).

If a small quantity of heat dQ is communicated to the mass without changing the weight m of the saturated vapor, we shall have the following changes produced:

First. The temperature of the liquid will increase by a small quantity dT. Hence if C denote the specific heat of the liquid at the temperature T (measured in kg. meters), then $(M - m)\,CdT$ will be equal to that part of dQ which is used up in raising the temperature of the liquid by dT.

Secondly. The temperature of the vapor is increased by the same amount dT. Hence its density will increase; and if we did not diminish the volume slightly by pushing down the piston, the weight m of the vapor part of our whole mass would increase. Supposing now that by a slight depression we keep m constant, there will be no vaporization and the rest of dQ will go to increase simply the temperature of the m kg. of the saturated vapor by dT degrees.

This point needs a little fuller discussion on account of its importance in the theory of the steam-engine. Suppose that we have 1 kilogramme of vapor in saturated state but not in contact with its own liquid, and that we wish to increase its temperature by dT degrees centigrade and still keep it saturated. We can proceed in the following way:

We communicate to it a quantity of heat dQ_1 which is just sufficient to raise its temperature by dT degrees. The vapor is then superheated, that is to say, its density is smaller than the density corresponding to its saturated state at that temperature $T + dT$. In order to increase the density so as to make it equal to the density of saturation at the temperature $T + dT$, we now compress it isothermally until the proper density is reached. Let the heat developed by this compression be dQ_2, then $dQ_1 - dQ_2 = $ the heat which must be supplied to 1 kg. of the saturated vapor in

order to raise its temperature by dT degrees and still keep the vapor saturated at this increased temperature.

$\dfrac{dQ_1 - dQ_2}{dT}$ is denoted by H and *called the specific heat* (in kg.-m.) *of saturated* vapor. It is evidently equal to the heat which would have to be supplied to one kilogramme of saturated vapor in order to raise its temperature by one degree and maintain it in saturated condition, if the ratio of the supply of heat to the rise of temperature remained constant.

Hence in our problem above the part of dQ which is expended in raising the temperature of the m kg. of saturated vapor without superheating and without increasing the quantity of m will be $mHdT$.

The total heat contained in the mass will be increased because the temperature of the mass is increased. The rate at which the heat of the mass increases with the increase of temperature, everything else remaining the same, is expressed in the well-known notation $\dfrac{\partial Q}{\partial T}$. Hence the increment in the heat due to the increment dT of the temperature is $\dfrac{\partial Q}{\partial T}dT$. This is evidently equal to the heats mentioned under 1 and 2. We can therefore write

$$\frac{\partial Q}{\partial T}dT = (M - m)CdT + mHdT,$$

or

$$\frac{\partial Q}{\partial T} = m(H - C) + MC.$$

Definitional Process (B).

Let the piston rise so as to allow a small quantity dm of the liquid to evaporate. In consequence of this evaporation the temperature of the mass begins to sink; we therefore supply heat in order to maintain it constant. Let dQ be equal to the heat supplied to the total mass during the isothermal evaporation of the quantity dm. The ratio $\dfrac{dQ}{dm}$ is denoted by ρ and called *the heat of evaporation*. It evidently means the number of units of heat which must be supplied, in order to evaporate isothermally one kg. of water at T' deg. centig., and the pressure of saturated vapor at that temperature into saturated vapor. Let $\dfrac{\partial Q}{\partial m}$ denote the rate at which the heat of the whole mass increases when the water is evaporated isothermally, then $\dfrac{\partial Q}{\partial m}dm$ is evidently the total increment of heat when dm unit weights of the liquid pass isothermally into that many units of saturated vapor. But we have just seen that this is also equal to ρdm. Hence

$$\frac{\partial Q}{\partial m}dm = \rho dm,$$

or

$$\frac{\partial Q}{\partial m} = \rho.$$

The two equalities obtained by the definitional processes (A) and (B) enable us now to deduce a very elegant statement of the two laws of thermodynamics for saturated vapors.

Forms of Statement of the Two Laws of Thermodynamics for Saturated Vapors.

We start with the general statements of these two laws:

$$dQ = dU + pdv$$

and

$$dQ = TdS \ . \ .$$

By carrying out the indicated differentiation, remembering that T and m are our variables—that is to say, remembering that Q, U, S, and v are in our discussion of saturated vapors functions of T and m and of nothing else—we obtain the following relations:

We commence with the first law.

$$\frac{\partial Q}{\partial T}dT + \frac{\partial Q}{\partial m}dm = \left(\frac{\partial U}{\partial T} + p\frac{\partial v}{\partial T}\right)dT + \left(\frac{\partial U}{\partial m} + p\frac{\partial v}{\partial m}\right)dm.$$

This is an identical equation in dm and dT; hence we must have, according to well-known rules in algebra,

$$\frac{\partial Q}{\partial T} = \frac{\partial U}{\partial T} + p\frac{\partial v}{\partial T},$$

$$\frac{\partial Q}{\partial m} = \frac{\partial U}{\partial m} + p\frac{\partial v}{\partial m}.$$

Comparing these two relations with the expressions for $\frac{\partial Q}{\partial T}$ and $\frac{\partial Q}{\partial m}$ obtained by the definitional processes (A) and (B), we infer that

$$\frac{\partial U}{\partial T} + p\frac{\partial v}{\partial T} = m(H - C) + MC,$$

$$\frac{\partial U}{\partial m} + p\frac{\partial v}{\partial m} = \rho.$$

It must be observed that these two equalities are nothing more nor less than a slightly different mathematical statement of the first law. Nor will any other mathematical relation which we can derive from these two equalities by any mathematical operations whatever contain a single grain of truth which is not already contained in the original statement of that law. What do we gain, then, by going through all these tedious mathematical operations? Do we arrive at a simpler statement of this law? No, we do not. Mathematically speaking, the expression

$$dQ = dU + pdv$$

is the simplest form in which that law can be stated. Before answering the above question let us first perform the last mathematical operation and obtain the final form of statement of the first law. Differentiate the first of the above equations with respect to m and the second with respect to T, and subtract the first from the second so as to eliminate U.

Remember, however, that p, H, M, and C are independent of m. We obtain

$$\frac{\partial \rho}{\partial T} - (H - C) = \frac{\partial}{\partial T}\left(p\frac{\partial v}{\partial m}\right) - \frac{\partial}{\partial m}\left(p\frac{\partial v}{\partial T}\right) = \frac{\partial p}{\partial T}\frac{\partial v}{\partial m}.$$

Remembering now that $v = um + M\sigma$, hence $\frac{\partial v}{\partial m} = u$, we obtain finally

$$\frac{\partial \rho}{\partial T} - (H - C) = u\frac{\partial p}{\partial T}. \quad \ldots \quad \text{(I)}$$

This is the statement of the first law of thermodynamics for saturated vapors at which we were aiming continually during our tedious mathematical transformations. Now in what respect is this statement superior to the general statement $dQ = dU + pdv$? Evidently in this: it contains nothing but physical constants of the liquid and its saturated vapor, most of which, as we shall presently see, are capable of exact experimental measurement. A very famous scientist said once that a department of human knowledge becomes an exact science when it can express its laws in terms of things which are capable of exact experimental measurement. The intrinsic energy U, to be sure, is a thing which we can and did express in terms of a definite unit, the kilogramme-meter; we can also give a perfectly satisfactory definition for it. We can evidently define it in two ways,

which we may call the *absolute* and the *relative method of definition.* The absolute definition describes U as the energy which we can obtain from the body by a series of processes which would reduce the body to a state in which its intrinsic energy is zero. The relative definition describes U as the energy which we can obtain from a body by a series of processes which will reduce the body to a state which we call the normal state; and we can select any state for our normal state. For instance, we can define the intrinsic energy of a kilogramme of saturated water-vapor at any temperature as the energy which we can obtain from it by reducing it to a kilogramme of water at 0° C. and a pressure equal to the tension of its saturated vapor at that temperature. Still, when it comes to exact experimental measurement it is not U that we measure but the physical constants ρ, H, C, and u, and from the measurements of these the relative value of U can then in a very limited number of cases be obtained by calculation. Hence the desirability of stating the first law of thermodynamics of saturated vapors in terms of these physical constants which are capable of exact experimental measurement instead of in terms of U, a quantity which is not capable of direct experimental measurement. It is clear now that the ultimate object of all our long mathematical operations was to rid ourselves by a process of elimination of the quantity U.

We proceed now to perform the same process of elimination on the general statement of the second law. Carrying out the differentiations indicated in

$$dQ = TdS$$

and remembering that T and m are our independent variables, we obtain

$$\frac{\partial Q}{\partial T}dT + \frac{\partial Q}{\partial m}dm = T\frac{\partial S}{\partial T}dT + T\frac{\partial S}{\partial m}dm.$$

This is an identical equation in dT and dm, and therefore the following relations will hold true:

$$\frac{\partial Q}{\partial T} = T\frac{\partial S}{\partial T},$$

$$\frac{\partial Q}{\partial m} = T\frac{\partial S}{\partial m}.$$

Comparing these two relations with those obtained by the definitional processes (A) and (B) we obtain

$$T\frac{\partial S}{\partial T} = m(H - C) + MC,$$

$$T\frac{\partial S}{\partial m} = \rho.$$

Differentiating now the first equation with respect to m and the second with respect to T and then subtracting the first from the second in order to eliminate S, we obtain

$$\frac{\partial S}{\partial m} = \frac{\partial \rho}{\partial T} - (H - C).$$

But since

$$T\frac{\partial S}{\partial m} = \frac{\partial Q}{\partial m} = \rho,$$

we obtain

$$\frac{\rho}{T} = \frac{\partial \rho}{\partial T} - (H - C). \quad . \quad . \quad . \quad . \quad \text{(II)}$$

This is our final statement of the second law of thermodynamics for reversible processes in saturated vapors. It contains, just like the statement (I) of the first law, a mathematical relation between the experimentally measurable physical constants of the liquid and its saturated vapor.

By combining (I) and (II) we obtain another very important relation between these constants, viz.,

$$\rho = Tu\frac{\partial p}{\partial T}. \quad . \quad . \quad . \quad . \quad . \quad \text{(III)}$$

Observation.—It is well to call your attention here to a remark which was made in connection with our deduction of the differential statement of the second law,

$$dQ = TdS,$$

from the integral statement

$$\int \frac{dQ}{T} = 0.$$

The remark was to the effect that the integral statement described the total effect of a series of processes which taken together constitute a reversible cycle, without telling us anything about the separate effects of each particular process of that series. The differential statement, on the other hand, describes completely every minute step in the progress of the reversible cycle. The relations (II) and (III) illustrate the truth of this remark very forcibly; for they tell us that during every interval of time, no matter how small, the reversible operations will progress in such a way as to maintain those relations between the physical constants and the variable co-ordinates of the liquid and its vapor which are given by (II) and (III). But do not forget that relation (II) and to same extent relation (III) also is only another way of stating the differential form of the second law,

$$dQ = TdS.$$

More than this. The integral statement limits us to the study of those cycles which are composed of reversible operations only. The differential statement enables us to break through these limits and study cycles consisting of operations some of which are not reversible. For it is evident that we can apply (II) and (III) to every reversible operation of the cycle, and the irreversible operations we can attack by the first law or in any other way that we may consider correct and convenient. This has a very important technical significance, for we shall presently see that the cyclic operations in those types of steam and other caloric engines which prevail to-day are by no means reversible in all their parts.

Since numerical values of the physical constants ρ, H, and C have been tabulated by various experimentalists in terms of the kg. calorie and not the kg. meter as the unit, it is advisable to substitute in our equations (I), (II), and (III) the numerical values of ρ, H, and C in terms of the kg. calorie as unit. Let

$r =$ the numerical value of ρ when the unit is a kg. calorie;
$c =$ " " " " C " " " " " " "
$h =$ " " " " H " " " " " " "

then

$$\frac{\rho}{J} = r, \quad \frac{C}{J} = c, \quad \frac{H}{J} = h;$$

hence we obtain from (I), (II), and (III) by these substitutions

$$\frac{\partial r}{\partial T} + c - h = \frac{u}{J}\frac{\partial p}{\partial T}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (\text{I}^{\text{a}})$$

$$\frac{\partial r}{\partial T} + c - h = \frac{r}{T}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (\text{II}^{\text{a}})$$

$$r = \frac{Tu}{J}\frac{\partial p}{\partial T} \quad \cdot \quad \cdot \quad \cdot \quad (\text{III}^{\text{a}})$$

These three equations are our fundamental equations in the thermodynamics of reversible processes in saturated vapors.

We now proceed to the next part of our programme, and

that is the numerical calculation of the physical constants of saturated vapors.

Numeral Calculation of the Physical Constants of Saturatfed Vapors.

Our three fundamental equations (I^a), (II^a), and (III^a) represent two independent relations [since (III^a) has been deduced from (I^a), that is the first law, and (II^a), that is the second law of thermodynamics] between five unknown quantities, viz., r, h, u, c, and $\dfrac{\partial p}{\partial T}$. Hence they enable us to calculate any two of these quantities when the remaining three are known. That is to say, three of these physical constants of saturated vapors must be determined experimentally and the other two can then be calculated by means of the fundamental laws of thermodynamics. What is meant by experimental determination is simply this: It must be found by experimental investigation in what way these physical constants depend on the variable co-ordinates of the body. In our discussion of the general physical properties of saturated vapors we saw that all the physical constants of such a vapor depend on the temperature only, hence the object of an experimental investigation will be to express these physical constants as functions of the temperature T. Three of the above constants having been experimentally determined, the remaining two can then be also expressed as functions of the temperature by simple calculation, starting with our fundamental equations (I^a), (II^a), and (III^a).

In most cases r, c, and p have been determined experiment-

ally, so that it is generally h and u, that is, the *specific heat* and the *specific volume of saturated vapors*, that we have to calculate.

We now proceed to carry out these calculations for a particular vapor, and select water vapor for reasons given above.

Regnault in his classical researches (Relation des expériences, Mém. de l'Acad. t. xxi, 1847, etc.) made the quantities c, r, and p, that is, the specific heat of water, the heat of evaporation, and the tension of saturated vapor of water, the subject of very careful experimental investigations. His results have been verified by all investigators in that field of physical research. We shall, therefore, use the values obtained from the results of his investigations.

The specific heat of water is expressed, according to Regnault's experimental data, by the following formula:

$$c = 1 + .00004t + .0000009t^2,$$

where t is the temperature in degrees centigrade above the freezing point.

For the heat of evaporation experimental data furnish the following relation:

$$r = 606.5 + .305t - \int_0^t cdt.$$

Substituting the value of c and carrying out the integration, we obtain

$$r = 606.5 - .695t - .00002t^2 - .0000003t^3.$$

For this long formula, Clausius (Mechanische Wärmetheorie, vol. i. p. 137) substitutes the following:

$$r = 607 - .708t.$$

To show the agreement between the values of r obtained from these two formulæ the following table is given for comparison:

t	0°	50°	100°	150°	200°
r according to Regnault's form.....	606.5	571.6	536.5	500.7	464.3
r " " Clausius' form......	607	571.6	536.2	500.8	465.4

The agreement is excellent. We shall, therefore, employ Clausius' simpler expression.

Taking the experimental data of Regnault's researches, Clausius [*] constructed the following table for the tension p of saturated water-vapor at various temperatures:

t in C. ° by Air Therm.	p in mm. of Hg.	t in C. ° by Air Therm.	p in mm. of Hg.
− 20	.91	110	1073.7
− 10	2.08	120	1489
0	4.60	130	2029
10	9.16	140	2713
20	17.39	150	3572
30	31.55	160	4647
40	54.91	170	5960
50	91.98	180	7545
60	148.79	190	9428
70	233.09	200	11660
80	354.64	210	14308
90	525 45	220	17390
100	760	230	20915

* Mechanische Wärmetheorie, vol. i. p. 149.

OBSERVATION 1. To transform p from pressure in mm. Hg to pressure in kg. per sq. m. we simply remember that 760 mm. barometric pressure is equivalent to 10,333 kg. per square meter. If we now wish to know how many kg. per sq. m. correspond to, say, 11,660 mm. barometric pressure, we simply put down the proportion

$$p : 10,333 :: 11,660 : 760,$$

where p is the pressure in kg. per sq. m., corresponding to 11,660 mm. barometric pressure.

$$p = \frac{10333 \times 1166}{76} = 158,530 \text{ kg. per sq. m.}$$

(about 229 pounds per square inch).

This, then, is the pressure of saturated water-vapor at 200° C.

OBSERVATION 2. · If we refer the tension p and the temperature t of the above table to a set of rectangular axes, measuring off t as the abscissæ and the corresponding p's as the ordinates, we obtain the curve as in diagram on opposite page.

The value of the differential coefficient $\frac{dp}{dt}$ $\Big($which is evidently the same as $\frac{dp}{dT}\Big)$ at any temperature represents the tangent of the angle which the tangent line to the curve at the point corresponding to that temperature makes with the axis of t. An inspection of the curve shows that this angle remains practically constant for considerable intervals of temperature, certainly for intervals of 10°.
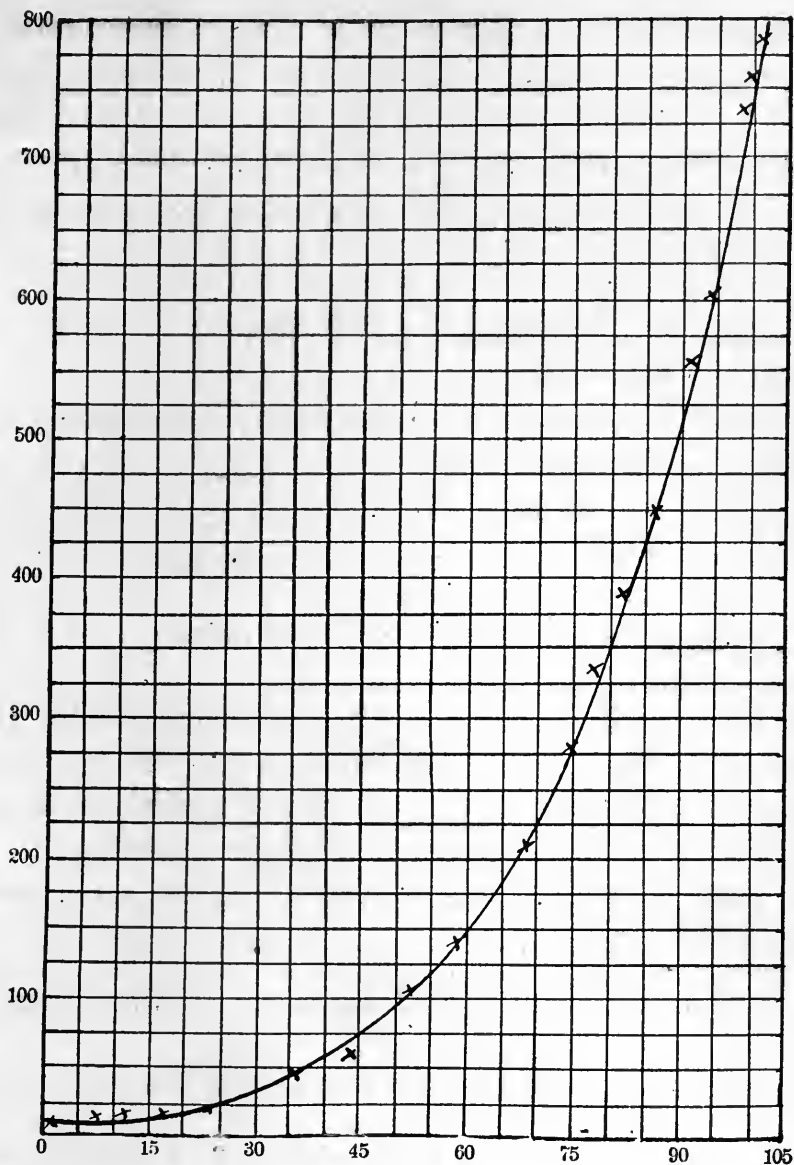
Consider now any interval of 10° and let

$$\frac{dp}{dt} = \alpha \text{ for that interval.}$$

$$\therefore \frac{1}{p}\frac{dp}{dt} = \frac{d}{dt}(\log p) = \frac{\alpha}{p} \text{ for the same interval.}$$

This relation enables us to calculate in a very simple manner the quantity $\dfrac{1}{p}\dfrac{dp}{dt}$ for any temperature. This is a quantity which we shall need presently. Suppose we wish to calculate $\left(\dfrac{1}{p}\dfrac{dp}{dt}\right)_{25}$, that is, the value of $\dfrac{1}{p}\dfrac{dp}{dt}$ for the temperature of $t = 25°$. We select, therefore, that 10° interval the mean temperature of which is 25°, that is, the interval between 20° and 30°. We obtain

$$\log p_{30} - \log p_{20} = \alpha \int_{20}^{30} \frac{dt}{p}.$$

The mean value of p within the limits of integration is very nearly the value of p at 25°, that is, p_{25}.

$$\therefore \log p_{30} - \log p_{20} = \frac{\alpha}{p_{25}} \int_{20}^{30} dt = \frac{\alpha 10}{p_{25}}.$$

But $\alpha = \left(\dfrac{dp}{dt}\right)_{25}$;

$$\therefore \frac{1}{p_{25}}\left(\frac{dp}{dt}\right)_{25} = \frac{\log p_{30} - \log p_{20}}{10} = \frac{\text{Log } p_{30} - \text{Log } _{20}}{M 10},$$

where Log stands for Briggs' logarithm, and M is the modulus of that system.

We are ready now to take up the calculation of the remaining physical constants, that is, to find the values of the

specific heat and the specific volume of saturated water-vapor for various temperatures within those limits within which the other physical constants were studied experimentally.

1. *Calculation of h.*

From the second law

$$\frac{dr}{dT} + c - h = \frac{r}{T},$$

we obtain

$$h = \frac{dr}{dt} + c - \frac{r}{t + 273}.$$

Regnault's experiments gave us

$$r = 606.5 + .305t - \int_0^t c\,dt.$$

$$\therefore \quad \frac{dr}{dt} = .305 - c.$$

Therefore

$$\frac{dr}{dt} + c = .305.$$

In the last term of the expression for h we shall substitute for r the simple expression given by Clausius and obtain

$$h = .305 - \frac{607 - .708t}{273 + t}.$$

The following table contains the calculated values of h for several temperatures:

t	0°	50°	100°	150°	200°
h	-1.916	-1.465	-1.133	$-.879$	$-.676$

The physical meaning of this negative specific heat will be considered further on in connection with adiabatic expansion of saturated water-vapor.

We pass on to the calculation of the specific volume of saturated water-vapor.

2. *Calculation of the Specific Volume of Saturated Water-vapor.*

The first question to consider is, whether in its saturated state water-vapor follows the law of Mariotte–Gay-Lussac, and if it does not, to what extent and in what way deviations occur.

Making use of the fundamental relation (III^a), we find, after replacing $(s - \sigma)$ for u,

$$r = \frac{T(s - \sigma)}{J} \cdot \frac{dp}{dt}$$

or

$$-\frac{273r}{T^2 \dfrac{1}{p}\dfrac{dp}{dt}} = \frac{273p(s-\sigma)}{J(273+t)}.$$

If the Mariotte–Gay-Lussac law were applicable to saturated water-vapor, then from $\frac{ps}{T} = $ const. we should have

$$\frac{ps \times 273}{J(273+t)} = \text{const.}$$

Since s differs but little from $(s-\sigma)$, we should have

$$\frac{p(s-\sigma)273}{J(273+t)} = \text{const.}$$

Comparing this to the equation just obtained from the fundamental relation (III^a), we see that if the Mariotte–Gay-Lussac law were applicable to saturated water-vapor we should have

$$\frac{273r}{T^2 \dfrac{1}{p}\dfrac{dp}{dt}} = \frac{p(s-\sigma)273}{J(273+t)} = \text{const.}$$

Having calculated $\frac{1}{p}\frac{dp}{dt}$ by the method described above, and r from the formula $r = 607 - .708t$, and substituted their

values in the last equation, Clausius obtained the following table:

$$\text{Table of } \frac{1}{J}p(s - \sigma)\frac{273}{273 + t}.$$

t in C.° by Air Thermometer.	Calculated from Regnault's data.	Calculated from Clausius' formula.
5	30.93	30.46
15	30.60	30.38
25	30.40	30.30
35	30.23	30.20
45	30.10	30.10
55	29.98	30.00
65	29.88	29.88
75	29.76	29.76
85	29.65	29.63
95	29.49	29.48
105	29.47	29.33
115	29.16	29.17
125	28.89	28.99
135	28.88	28.80
145	28.65	28.60
155	28.16	28.38
165	28.02	28.14
175	27.84	27.89
185	27.76	27.62
195	27.45	27.33
205	26.89	27.02
215	26.56	26.68
225	26.64	26.32

The figures given in the column headed "Calculated from Clausius' formula" will be explained presently.

We can easily see from this table that the Mariotte–Gay-Lussac law does not hold true; for $\frac{1}{J}p(s - \sigma)\frac{273}{273 + t}$ diminishes steadily with the increase of temperatures; *evidently because the specific volume of saturated steam diminishes more rapidly than the pressure increases with increase of temperature.* Clausius found that this formula could be reduced to the more simple one, viz.,

$$\frac{1}{J}p(s - \sigma)\frac{273}{273 + t} = m - ne^{at},$$

$$\text{where} \quad m = 31.549,$$
$$n = 1.0486,$$
$$\alpha = .007138.$$

By means of this formula Clausius calculated the figures given in the column headed "Calculated from Clausius' formula."

After this brief digression we return to the calculation of the

Specific Volume of Saturated Steam.

We had

$$\frac{1}{J}p(s - \sigma)\frac{273}{273 + t} = m - ne^{at}.$$

Since we commit an error of a small fraction only of one per cent by neglecting σ in comparison with s, we may write

$$s = \frac{J}{p}(m - ne^{at})\frac{273 + t}{273}.$$

Let $v' =$ volume of a kilogr. of air at a pressure p and temperature t, then will

$$v' = \frac{R'}{p}(273 + t);$$

$$\therefore \frac{s}{v'} = \frac{J}{R'}(m - ne^{at})\frac{1}{273}.$$

For a given temperature t, say the freezing temperature, this ratio can be determined experimentally, as will be explained presently.

Denoting the ratio $\frac{s}{v'}$ at the freezing temperature by $\left(\frac{s}{v'}\right)_0$, we shall have

$$\left(\frac{s}{v'}\right)_0 = \frac{J}{R'}(m - n)\frac{1}{273};$$

$$\therefore \frac{s}{v'} = \left(\frac{s}{v'}\right)_0 \frac{m - ne^{at}}{m - n}.$$

The value of $\left(\frac{s}{v'}\right)_0$ can be obtained easily by the following method:

Experiment tells us that saturated water-vapor at low temperatures obeys the Mariotte–Gay-Lussac law so nearly that we may use the law in practical calculations without committing an appreciable error. On that hypothesis the density of steam at 0° C. is easily obtained.

2 cub. m. H at 0° C. at a given pressure weigh $2 \times .06926$ as much as 1 cub. m. of air at the same temperature and pressure;

1 cub. m. O at 0° C. at a given pressure weighs 1×1.1056 as much as 1 cub. m. of air at the same temperature and pressure;

At low temperature, 2 cub. m. H and 1 cub. m. O unite into 2 cub. m. saturated water-vapor (very nearly).

∴ 2 cub. m. H_2O at 0° C. at a given pressure weigh $2 \times .06926 + 1.1056$ as much as 1 cub. m. of air at the same temperature and pressure;

1 cub. m. of H_2O at 0° C. at a given pressure weighs $\dfrac{2 \times .06926 + 1.1056}{2}$ as much as 1 cub. m. of air at the same temperature and pressure.

$$\therefore \left(\frac{s}{v'}\right)_0 = \frac{1}{\frac{1}{2}(2 \times .06926 + 1.1056)} = \frac{1}{.622}.$$

Therefore

$$\frac{s}{v'} = \frac{1}{.622} \frac{m - ne^{at}}{m - n},$$

which can also be expressed by a more convenient formula given by Clausius, thus:

$$\frac{s}{v'} = M - N\beta^t.$$

In this formula

$$M = 1.663,$$
$$N = .05527,$$
$$\beta = 1.007164.$$

This formula was used by Clausius to calculate the specific volume of saturated water-vapor at various temperatures. The results are given in the table on page 85. Parallel with these figures are given the figures obtained experimentally by two English engineers, Fairbairn and Tate.[*]

It must be observed that for every temperature we must 'know first the pressure of saturated vapor at that temperature, and, inserting that pressure in $pv' = RT$, calculate v'.

Observe the close agreement between experiment and theory as worked out by Clausius; *observe also the enormous increase of the density of steam with rising temperature.*

There is a temperature at which the density of steam is the same as that of water at the same temperature. This is called the *critical temperature* of water. Above the critical temperature the vapor cannot be liquefied by pressure alone.

It is highly probable that all bodies have a critical tem-. perature. In the case of the so-called perfect gases the criti-

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[*] Transactions of the Royal Society of London, 1860, vol. 150, p. 185.

Table of Specific Volume of Saturated Water-vapors.

t in C.°	From Clausius' Form.	Fairbairn and Tate's Experimental Table.
58.21	8.23	8.27
68.52	5.29	5.33
70.76	4.83	4.91
77.18	3.74	3.72
77.49	3.69	3.71
79.40	3.43	3.43
83.50	2.94	3.05
86.83	2.60	2.62
92.66	2.11	2.15
117.17	0.947	0.941
118.23	0.917	0.906
118.46	0.911	0.891
124.17	0.769	0.758
128.41	0.681	0.648
130.67	0.639	0.634
131.78	0.619	0.604
134.87	0.569	0.583
137.46	0.530	0.514
139.21	0.505	0.496
141.81	0.472	0.457
142.36	0.465	0.448
144.74	0.437	0.432

cal temperature is very low; hence the necessity of cooling in the liquefaction of gases.*

We now come to the *last and most important part of our discussion* of the application of the two laws of thermo-dynamics to the study of reversible processes in saturated vapors in general and water-vapor in particular, that is, to the *discussion of adiabatic and isothermal expansion of saturated vapors.*

* See the researches of Avenarius in Poggendorf's Annalen, 1874.

Adiabatic Expansion of Saturated Water-vapor.

We commence with the deduction from our fundamental relations of a mathematical expression which simplifies considerably our discussion of adiabatic expansion.

By the definitional processes (A) and (B) we obtained

$$\frac{\partial Q}{\partial T} = m(H - C) + MC,$$

$$\frac{\partial Q}{\partial m} = \rho;$$

$$\therefore dQ = \frac{\partial Q}{\partial T}dT + \frac{\partial Q}{\partial m}dm = \{m(H - C) + MC\}dT + \rho dm.$$

From the second law (Fundamental Relation II) we obtain

$$H - C = \frac{\partial \rho}{\partial T} - \frac{\rho}{T}.$$

Substituting this value of $(H - C)$ in the last equation, we derive the relation

$$dQ = \left\{ m\left(\frac{\partial \rho}{\partial T} - \frac{\rho}{T}\right) + MC \right\} dT + \rho dm.$$

Considering now that ρ, the heat of evaporation, depends on temperature only, it is evident that

$$\frac{\partial \rho}{\partial T}dT = d\rho;$$

$$\therefore \ m\frac{\partial \rho}{\partial T}dT + \rho dm = md\rho + \rho dm = d(m\rho);$$

$$\therefore \ dQ = d(m\rho) + \left(MC - \frac{m\rho}{T}\right)dT,$$

or

$$dQ = Td\left(\frac{m\rho}{T}\right) + MCdT.$$

This is the expression which we started out to deduce.
In adiabatic expansion $dQ = 0$, hence

$$Td\left(\frac{m\rho}{T}\right) + MCdT = 0,$$

or

$$Td\left(\frac{mr}{T}\right) + McdT = 0;$$

$$\therefore \ \frac{mr}{T} - \frac{m_1 r_1}{T_1} = - M\int_{T_1}^{T}\frac{cdT}{T}.$$

Calculation is simplified very much and the error com-
mitted is very small if we put $c = $ constant, during the expan-
sion, provided that the expansion does not extend over a very
large interval of temperature. In practice this never occurs.

$$\therefore \ \frac{mr}{T} - \frac{m_1 r_1}{T_1} = + Mc \log \frac{T_1}{T},$$

or

$$m = \frac{T}{r}\left\{\frac{m_1 r_1}{T_1} + Mc \log \frac{T_1}{T}\right\}.$$

(α) *Condensation during Adiabatic Expansion of Saturated Water-vapor.*

A very interesting but, from an economical standpoint, a very objectionable phenomenon takes place when saturated water-vapor expands adiabatically. Owing to the fact that during such an expansion the temperature (in consequence of external work done by the expansion) sinks more rapidly than the density diminishes, the vapor condenses. Hence in order to prevent this condensation it would be necessary to supply heat during the expansion. *This, then, is the physical meaning of the negative specific heat,* as found above, *of saturated water-vapor.* During adiabatic compression the vapor would, of course, become superheated. The last equation enables us to calculate the amount of this condensation. For example, suppose that m_1 kilogrammes of saturated water-vapor at initial temperature T_1 are enclosed in a cylinder by a piston which can glide up and down without friction. Let there be no liquid mass in the cylinder. Hence $M = m_1$, and as the piston goes up slowly owing to the gradual diminution of the pressure, we shall have at any moment

$$\frac{m}{m_1} = \frac{T}{r}\left(\frac{r_1}{T_1} + c \log \frac{T_1}{T}\right).$$

Starting with initial temperature $T_1 = 150° + 273$, Clausius[*] calculated the ratio of the vapor weight m at various temperatures T to the initial weight m_1. The following table contains the interesting results of this calculation:

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[*] Mechanische Wärmetheorie, vol. i. p. 164.

t	150°	125°	100°	75°	50°	25°
$\dfrac{m}{m_1}$	1	.956	.911	.866	.821	.776

The amount of condensation is, therefore, very considerable.

This phenomenon contributes to what is known in steam-engineering under the name of *cylinder condensation,* a process which, as is easily seen, pulls down the output of the steam-engine. Other and probably quite as serious caus s contribute to this objectionable process in the cylinder of a steam-engine. Various devices have been suggested and tried in order to overcome this evil, but the discussion of these is outside of the limits of this course.

(β) *Calculation of the External Work done during an Adiabatic Expansion.*

$$W = \int_{v_1}^{v} p\,dv.$$

But $v = mu + M\sigma$.

$$\therefore \ p\,dv = p\,d(mu) = d(mup) - mu\frac{\partial p}{\partial T}dT.$$

From our fundamental equation (III) we have

$$\rho = Tu\frac{\partial p}{\partial T}.$$

$$\therefore \ p\,dv = d(mup) - \frac{m\rho}{T}dT,$$

Since v changes adiabatically, we can make use of the relation deduced in the last paragraph when we considered the process of condensation during adiabatic expansion. The relation is

$$Td\left(\frac{m\rho}{T}\right) + MCdT = 0,$$

or

$$\frac{m\rho}{T}dT - d(m\rho) = MCdT.$$

$$\therefore pdv = d(mup) - d(m\rho) - MCdT.$$

$$\therefore W = \int_{v_1}^{v} d(mup) - \int_{v_1}^{v} d(m\rho) - MC\int_{T_1}^{T} dT$$

$$= mup - m_1u_1p_1 - [m\rho - m_1\rho_1] + MC(T_1 - T).$$

Since the quantities ρ and C are given, by the experimental formulæ discussed above, in kg.-calories, it is preferable to express W thus:

$$W = mup - m_1u_1p_1 - J\{(mr - m_1r_1) - Mc(T_1 - T')\}.$$

This formula enables us to calculate the external work W in kg.-meters when a certain initial quantity m_1 of saturated water-vapor at temperature T_1, being in contact with a quantity $M - m_1$ of its own liquid at the same temperature, expands adiabatically until its temperature has gone down to a temperature T. Thus:

Since T_1 and T are given, p_1 and p can be found by a reference to Regnault's table of vapor tensions. Since m_1 and M are also given, $JMc(T_1 - T)$ and Jm_1r_1 can be easily calculated. There still remain mr and mu to be calculated. The quantity mr we have already calculated in the preceding paragraph and found

$$mr = T\left(\frac{m_1 r_1}{T_1} - Mc \log \frac{T}{T_1}\right).$$

The quantity mu can be easily found thus:
From the fundamental relation (III^a) we have

$$mr = mu\frac{T}{J}\frac{dp}{dT}.$$

Substituting this value of mr in the last equation, we obtain

$$mu = \frac{J}{\dfrac{dp}{dT}}\left(\frac{m_1 r_1}{T_1} - Mc \log \frac{T}{T_1}\right).$$

The quantity $\frac{dp}{dT}$ is the tangent of the angle which the tangent line to the curve of vapor tension, given above, at the point corresponding to temperature $T = 273 + t$, makes with the axis of t, and can be easily found either graphically or by calculation, thus:

Suppose we wish to calculate $\frac{dp}{dT}$ for the temperature

$t = 110°$. On account of the gradual ascent of the curve of vapor tension, we have

$$\left(\frac{dp}{dt}\right)_{110} = \frac{p_{220} - p_{110}}{10}.$$

Referring now to Regnault's table we find p_{120} in mm. $= 1489$ and p_{110} in mm. $= 1073.7$. Hence, according to the explanation given before, in order to transform these pressures into kg. per square m. we have to divide by 760 and multiply by 10,333. We obtain

$$\left(\frac{dp}{dt}\right)_{110} = \frac{(1489 - 1073.7)\frac{10333}{760}}{10} = 564.64.$$

It is seen, therefore, that the two laws of thermodynamics in connection with the experimental data on saturated water-vapor enable us to calculate all the quantities which enter into the expression for the external work done by the adiabatic expansion of such a vapor.

It should be noticed that this expression is very much different from the corresponding expression obtained for the adiabatic expansion of a perfect gas. This difference would not exist if saturated vapors obeyed the law of Mariotte–Gay-Lussac.

The following table is taken from Clausius[*]; its verification is recommended as a very useful exercise. It contains the external work per kg. of saturated vapor when the initial temperature is $t = 150°$ C. and the initial quantity of the liquid part is zero, hence $M = m_1$.

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[*] Mech. Wärmetheorie, vol. i. p. 167.

t	150°	125°	100°	75°	50°	25°
$\dfrac{W}{m_1}$	0	11,300	23,200	35,900	49,300	63,700

Thus the external work done by a kg. of saturated water-vapor in expanding adiabatically from initial temperature of $t = 150°$ C. until its temperature has sunk down to $100°$ C. is 23200 kg. meters.

OBS. 1. In evaporating a kg. of water at $150°$ to a kg. of steam at $150°$ work must be done against the vapor pressure corresponding to that temperature. This work can be easily found to be 18,700 kg. meters.

OBS. 2. In the above calculation Clausius assumed $J = 423.55$.

(γ) *External Work done during Isothermal Expansion.*

During isothermal expansion pressure remains constant, since temperature remains constant. The heat supplied is utilized to compensate two distinct processes which, taken together, constitute the operation of isothermal expansion. The two processes are: separation of the vapor from the liquid mass, and overcoming of the external pressure. According to our definition of ρ, that is, the latent heat of evaporation, the total heat necessary to evaporate m kilogrammes of vapor is $m\rho$. That part of this total heat which does the external work is given by

$$W = \int p\, dv.$$

But $v = mu + M\sigma$, and in isothermal expansion

$$dv = \frac{\partial v}{\partial m}dm = udm.$$

$$\therefore \ W = \int_0^m pudm = pum,$$

since p and u remain constant during this expansion

We are ready now to take up the discussion of a complete cycle of operations upon water-vapor.

THE INDICATOR DIAGRAM OF A SIMPLE CYCLE.

We shall arrange the cycle in such a way that it shall approach as nearly as possible the cycles which occur in actual steam-engines, without introducing the difficult questions concerning the various causes which produce considerable differences between the results obtained by pure theory and the results obtained from the actual operation of the various types of steam-engines. The existence of these differences is no proof of the weakness of the fundamental features of our theory. On the contrary, these very differences prove its strength, for they point out the important fact that some of the changes or phenomena which take place during the cyclic operations of actual steam-engines have not been taken into account in our theoretical calculations. Careful experimental investigations of these ignored phenomena and the study of their bearing upon the performance of the steam-engine, not only mean the gradual extension towards a complete theory

of the steam-engine, but they also, by widening out that theory, bring us nearer and nearer to a perfect steam-engine.

Fig 9 represents symbolically the essential parts of a modern steam-engine. A is the boiler, maintained at constant temperature T_1 by the action of the heat supplied by fuel. C is the condenser maintained at constant tempera-
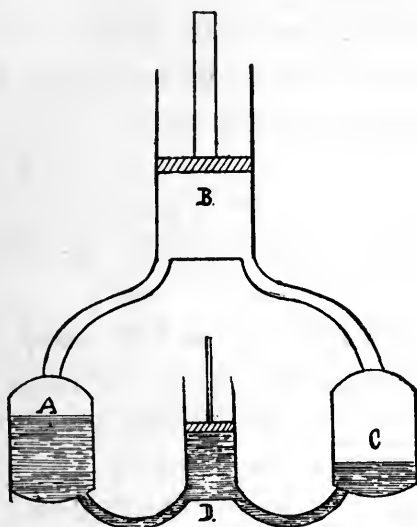

Fig. 9.

ture T_0. To simplify our discussion, we shall suppose that the condenser is maintained at constant temperature by taking away all the heat that may be supplied to it during the cycle which we are considering, and not by injection of cold water. B is the cylinder in which a piston can glide up and down without friction. We shall suppose that the cylinder is impermeable to heat. The action of the pump D will be explained presently. We shall now suppose that by special mechanical contrivances we can at any moment connect the

cylinder to or disconnect it from either the boiler A or the condenser C.

Operation 1.

At the beginning of the cycle the piston is at the bottom of the cylinder. Steam is now admitted from the boiler, and when its quantity is m_1 the connection with the boiler is cut off. Suppose that a quantity of the liquid equal to $M - m_1$ also enters with the steam. The piston goes up until the volume v_1 in the cylinder is

$$v_1 = m_1 u_1 + M\sigma.$$

Since the pressure during this operation is constant and equal to p_1, (the saturated-vapor tension at the initial temperature T_1), the external work W_1 done during this operation is given by

$$W_1 = p_1(m_1 u_1 + M\sigma).$$

The quantity of heat Q_1 consumed during this isothermal expansion is $m_1 \rho_1$.

In order to represent the cycle graphically, refer the pressures on the piston and the volume in the cylinder to a set of rectangular axes OA and OB, taking the pressures in kg. per sq. m. for ordinates and the corresponding volumes in cub. m. for abscissæ (Fig. 10*).

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*This diagram was taken from an actual steam-engine. Boiler gauge, 165; vacuum gauge, 12.75; rev. per minute, 76; back pressure, 17 lbs.

The first operation will be represented by the isothermal line ab. The length of $ab = Ob'$ represents the numerical

FIG. 10.

value of $v_1 = m_1 u_1 + M\sigma$. The area $abb'O$ is numerically equal to W_1.

Operation 2.

Disconnect the cylinder from the boiler, and by gradually diminishing the pressure let the steam expand from this point on adiabatically until its temperature has sunk to T_2, the temperature of the condenser. During this operation the steam, as was explained before, not only remains saturated but even condenses rapidly. The adiabatic curve will be somewhat like the curve bc. Its exact form can be traced very accurately by theoretical calculation, but since this is a somewhat tedious process we shall omit it from our discussion. The external work done during this operation is represented by the area $bcc'b'$. Denoting it by W_2 we shall have, as has been shown before,

$$W_2 = m_2 u_2 p_2 - m_1 u_1 p_1 - J\{(m_2 r_2 - m_1 r_1) - Mc(T_1 - T_2).\}.$$

Operation 3.

Connect the cylinder with the condenser and compress. The initial volume in the cylinder is

$$v_2 = (m_2 u_2 + M\sigma).$$

Let the connection with the condenser be maintained until the piston reaches its initial position again. Since the pressure during this operation remains constant and equal to p_2, the work done during this operation will be, denoting it by W_3,

$$W_3 = -p_2 v_2 = -p_2(m_2 u_2 + M\sigma).$$

The curve of compression cd is an isothermal ; it is evidently a straight line parallel to OB. The area $CC'Od$ represents numerically the value of W_3.

This operation completes the cycle as far as the process in the cylinder is concerned. The diagram $abcd$ is called the *indicator diagram* of the cycle. Its area is numerically equal to the external work done during the cyclic process. Let this be W, then

$$W = W_1 + W_2 + W_3$$

$$= [p_1(m_1 u_1 + M\sigma)] + [m_2 u_2 p_2 - m_1 u_1 p_1 - J\{(m_2 r_2 - m_1 r_1) - Mc(T_1 - T_2)\}] + [-p_2(m_2 u_2 + M\sigma)]$$

$$= M\sigma(p_1 - p_2) + JMc(T_1 - T_2) - J(m_2 r_2 - m_1 r_1).$$

Corrections for the Work expended upon the Pump.

The cycle given above is not complete because the state of the boiler and condenser is not the same at the end of the cycle as in the beginning of it. In the first place, the quantity of the water in the condenser is increased and that in the boiler diminished by M kilogrammes. To make the cycle complete it is necessary now to transfer this quantity M from the condenser to the boiler by the action of the pump. The work of the pump subtracted from W gives us then the available external work of the complete cycle.

The work of the pump is easily calculated thus :

In order to transfer the quantity M from the condenser to the pump the piston of the pump must go up until it has increased the available volume in the cylinder of the pump by $M\sigma$. During the upward stroke of the latter's piston a valve connects the pump to the condenser, and the condenser pressure p_2 forces the quantity M into the cylinder. The work of the pressure p_2 will evidently be

$$W_4 = p_2 M\sigma.$$

The valve connecting the pump to the condenser is then turned off, and another valve is turned on which connects the pump to the boiler. The piston of the pump is now pressed down and the quantity M of the fluid is forced into the boiler against the pressure p_1. This work is evidently

$$W_5 = - p_1 M\sigma.$$

Adding $W_4 + W_5$ to W will give us W', that is, the *available* external work done during the complete cycle.   Hence

$$W' = JMc(T_1 - T_2) - J(m_2 r_2 - m_1 r_1).$$

The quantity of heat expended so far to gain this amount of external work is $m_1 r_1$.   But this is not all.   For in order to establish the same state of the boiler and condenser as at the beginning of the cycle it is necessary to heat the quantity M of the liquid, after it enters the boiler again, from the temperature T_2 to the temperature T_1, for which an additional quantity of heat, $MC(T_1 - T_2)$, is required.   We have therefore on the whole a gain of W' units of available external work at the expense of (very nearly) $J\{m_1 r_1 + Mc(T_1 - T_2)\}$ units of heat.

$$\frac{W'}{J[m_1 r_1 + Mc(T_1 - T_2)]} = \text{efficiency} = E,$$

or

$$\frac{Mc(T_1 - T_2) + m_1 r_1 - m_2 r_2}{Mc(T_1 - T_2) + m_1 r_1} = E.$$

Calculation of the Efficiency in Terms of the Initial and Final Temperatures.

In order to obtain a more suggestive comparison of this result to the result which we obtained in the case of a simple reversible cycle with a perfect gas, it is desirable to express E in terms of initial and final temperature.   The second opera-

tion being an adiabatic expansion, we have the following relation :

$$m_2 r_2 = T_2 \left(\frac{m_1 r_1}{T'} - Mc \log \frac{T_2}{T_1} \right).$$

Substituting this value of $m_2 r_2$ in the expression for E, we obtain

$$E = \frac{Mc \left(T_1 - T_2 + T_2 \log \frac{T_2}{T_1} \right) + m_1 r_1 \dfrac{T_1 - T_2}{T_1}}{Mc(T_1 - T_2) + m_1 r_1}.$$

To simplify this equation somewhat, suppose that at the beginning of the cycle no part of the mass is liquid. Hence

$$m_1 = M,$$

and

$$E = \frac{T_1 c \left(1 + \dfrac{T_2}{T_1 - T_2} \log \frac{T_2}{T_1} \right) + r_1}{c(T_1 - T_2) + r_1} \cdot \frac{T_1 - T_2}{T_1}$$

$$= \left\{ 1 - \frac{T_2 c \left(\dfrac{T_1}{T_1 - T_2} \log \frac{T_1}{T_2} - 1 \right)}{c(T_1 - T_2) + r_1} \right\} \frac{T_1 - T_2}{T_1}.$$

It can be easily shown that $\left(\dfrac{T_1}{T_1 - T_2} \log \frac{T_1}{T_2} \right)$ is always greater than unity as long as $T_2 < T_1$. Hence the efficiency of our cycle is smaller than that of a simple reversible cycle performed upon a perfect gas. Now the efficiency of a

SUMMARY.

1. *Method of Reasoning which led to the General Form of the Second Law of Thermodynamics.*

After discussing the application of the first law of thermodynamics to the study of reversible operations performed upon perfect gases we passed on to a similar discussion for the next simplest class of bodies, that is, saturated vapors. We suggested, however, that it would be advisable to deduce first another general law which, together with the first law, forms the foundation of the science of thermodynamics: we mean the second law. In doing that we followed practically in the steps of the great Carnot. For he had to discover the second law before he was able to pass from the study of the reversible gas-engine to that of the steam-engine.

The first and simplest form of the second law was obtained by considering the efficiency of a Carnot engine operating reversibly upon a perfect gas by simple cycles. This form consisted in a mathematical statement which expressed that the efficiency of such cycles depends on the extreme temperatures of the cycles, thus:

$$\frac{Q}{Q_1} = \frac{T_1 - T_2}{T_1}.$$

We then introduced the *axiom of Clausius* and by means of this axiom we showed that *the efficiency of a simple reversible cycle is independent of the substance operated upon.* Hence it is always

$$\frac{Q}{Q_1} = \frac{T_1 - T_2}{T_1}.$$

We then transformed this relation into the following:

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0.$$

It was stated that this transformed expression is preferable because it lends itself more readily to generalization. In order to effect this generalization we passed on to the consideration of a *complex reversible cycle* and obtained the relation

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} + \frac{Q_3}{T_3} + \ldots + \frac{Q_n}{T_n} = 0,$$

or

$$\Sigma \frac{Q}{T} = 0.$$

We finally considered a reversible cycle of *infinite complexity* and obtained

$$\int \frac{dQ}{T} = 0,$$

where the integral is to be extended all around the closed curve which represents graphically the reversible cycle of infinite complexity, that is to say, all around the *indicator diagram.*

This is the *integral form of the second law for reversible cycles.* But inasmuch as the integral laws in general describe resultant effects only of a series of physical processes and throw but very little light upon each process of that series, we

proceeded to deduce from the integral law $\int \dfrac{dQ}{T} = 0$ a differential law, that is to say a relation which will hold true during every interval, no matter how small, of the entire time during which the cyclic process is completed.   We obtained

$$\frac{dQ}{T} = dS.$$

That is to say, the heat absorbed by a body during any one of the infinite number of infinitely small operations which taken together form the complete reversible cycle is equal to the absolute temperature of the body multiplied by the increment of the *entropy* of the body.   The definition of the entropy being: 1st. *Mathematical* and complete. It is a finite, continuous, and singly-valued function of the co-ordinates which define the state of the body, that is, of pressure, volume, and temperature, which satisfies the above differential equation for any reversible operation. 2d. *Physical* meaning. Its variation during an isothermal operation is equal to the heat absorbed or given off, divided by the absolute temperature at which the operation takes place.   Its variation is zero during an adiabatic operation.

2. *Forms of the Two Laws in the case of Reversible Operations on Saturated Vapors.*

Starting, then, with our two laws of thermodynamics,

$$dQ = dU + pdv,$$

$$dQ = TdS,$$

we took up the discussion of saturated vapors, and in this discussion we followed up as much as possible the line of reasoning which we employed in the discussion of reversible processes in perfect gases.

1st. We discussed the most essential physical properties of saturated vapors by consulting carefully the records of physical research.

2d. We then performed two simple processes for the purpose of defining the physical constants of a saturated vapor. These two processes we called the definitional processes (A) and (B). They gave us the following two definitional relations:

$$\frac{\partial Q}{\partial T} = m(H - C) + MC,$$

$$\frac{\partial Q}{\partial m} = \rho.$$

These two definitional relations enabled us then to express the two laws of thermodynamics in the case of saturated vapors in a very convenient form, viz.,

$$\frac{\partial \rho}{\partial T} + C - H = u\frac{\partial p}{\partial T}, \quad \cdots \cdots \text{(I)}$$

$$\frac{\partial \rho}{\partial T} + C - H = \frac{\rho}{T}, \quad \cdots \cdots \text{(II)}$$

and by combining these two we obtained a third very convenient relation:

$$\rho = Tu\frac{\partial p}{\partial T}. \quad \cdots \cdots \text{(III)}$$

By introducing the kg. calorie as the unit of heat (as is generally done in experimental researches) we obtained

$$\frac{\partial r}{\partial T} + c - h = \frac{u}{J}\frac{\partial p}{\partial T}, \quad \cdots \cdots \quad \textbf{(I^{a})}$$

$$\frac{\partial r}{\partial T} + c - h = \frac{r}{T}, \quad \cdots \cdots \quad \textbf{(II^{a})}$$

$$r = \frac{Tu}{J}\frac{\partial p}{\partial T}. \quad \cdots \cdots \quad \textbf{(III^{a})}$$

3. *Application of the Two Laws to the Study of the Physical Constants of Saturated Vapor.*

We then proceeded to apply these fundamental thermodynamical relations to the study of saturated vapors, and in particular to the study of saturated water-vapor. We divided this discussion into three parts. One part related to the discussion of the constants c, h, r, u, and p, especially to the methods of calculating two of them, h and u, when the other three are given by experimental data. The negative value of the specific heat, the increase of density with the temperature, and the deviation of the behavior of saturated water-vapor from the law of Mariotte–Gay-Lussac were discussed with particular emphasis.

4. *Application of the Two Laws to the Study of Isothermal and Adiabatic Expansion of Saturated Water-vapor.*

Following the method of discussion which we employed in the case of perfect gases we then took up the very important

part of our work in thermodynamics, that is, adiabatic and isothermal expansion of saturated water-vapor, the *condensation which takes place during adiabatic expansion* and the *superheating which takes place during adiabatic compression* were particularly dwelt upon. The external work done during adiabatic and isothermal operations received our most careful attention.

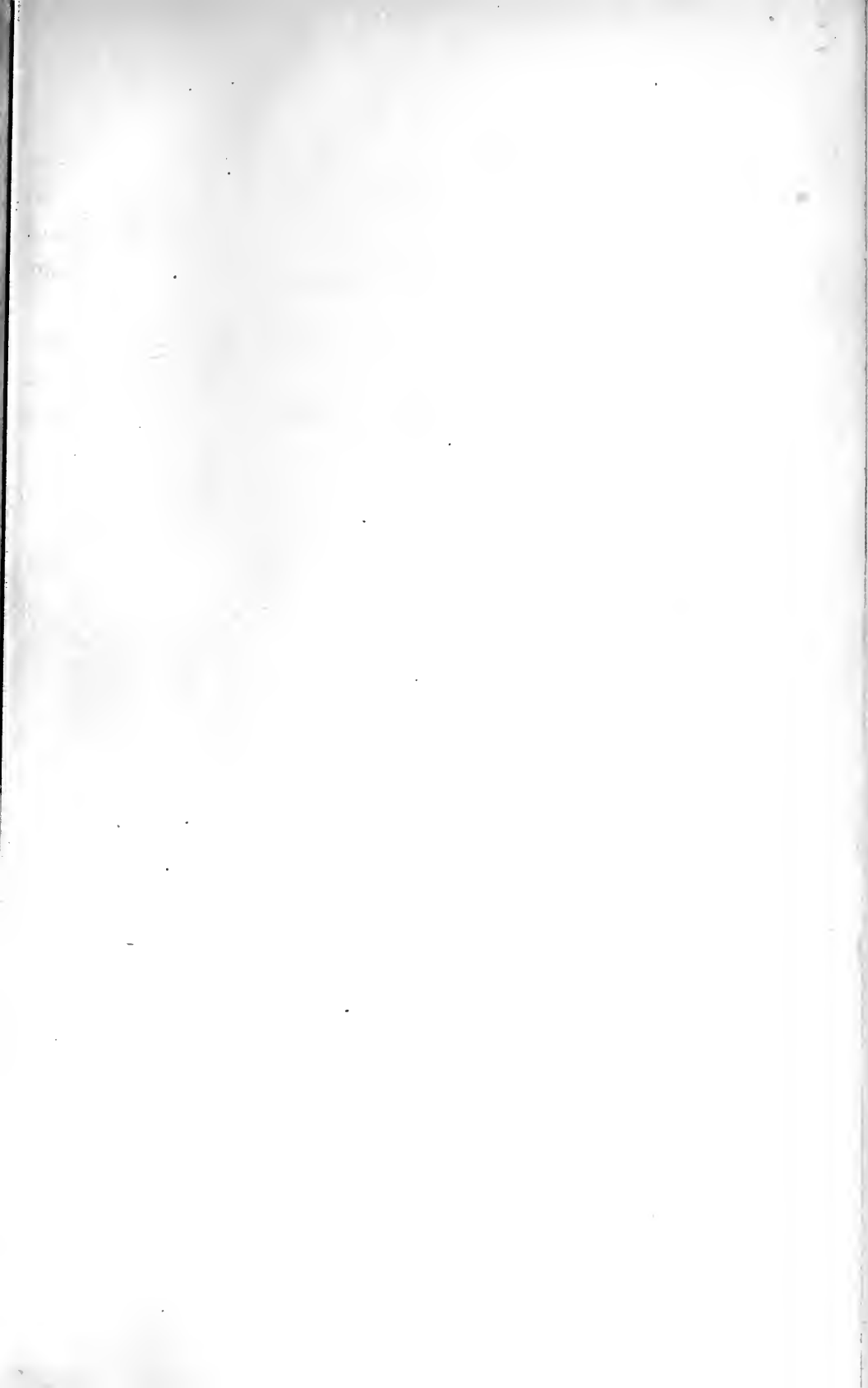### 5. *Non-reversible and Reversible Cycles of Operation upon Saturated Water-vapor.*

We were ready then to take up the question of the theoretical efficiency of the non-reversible and the reversible types of steam-engines. This question is, from an engineering standpoint, the most important of all questions in thermodynamics. It is also exceedingly important from a historical point of view, for the study of this question led Carnot to the discovery of the two laws of thermodynamics.

The external work done during each component operation of these cycles was calculated and expressed by formulæ which admit of being reduced to actual figures, so that the action of each component operation could be studied by finding the numerical value of this action in terms of kg. meters. The theoretical efficiency of non-reversible machines was then shown to be smaller than that of the reversible type, and the efficiency of this was then demonstrated by actual calculation to be the same as that of a Carnot reversible engine operating by simple reversible cycles upon a perfect gas.

There remains still another important application of the two laws of thermodynamics which is within the limits of

this purely theoretical course. It is the application to the study of *the flow of gases and vapors.* In this part of our discussion we propose to follow closely the beautifully worked out Chapter IX in Peabody's "Thermodynamics of the Steam-engine."

These are the most essential elements of theoretical thermo-dynamics, upon which as a strong foundation the practical engineer must raise the vast structure of the beautiful science of Caloric Engineering.